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Light Barrier for Non-Foil Packaging

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13. ABSTRACT (Maximum 200 words) Light barrier requirements for all-polymeric high oxygen and water vapor barrier (OTR and WVTR respectively) flexible pouch laminations were evaluated for use in a thermal Microwave sterilization (MWS) process suitable for low acid canned foods. The US Army OTR specification for flexible pouches can be satisfied by all polymeric multi-layered barrier materials, but WVTR is five (5) to ten (10) times the US Army specification. A method was developed to quantify both the dielectric constant and the dielectric loss factor for the polymeric multi-layered barrier materials. Attempts to increase water barrier performance using nanoclay particles dispersed in polyolefin sealant layers did not succeed in reaching specified levels. Multilayered material was used successfully to package US Army MRE cheese sauce, dessert bar and chicken and dumplings entrée items. Chicken and dumplings entrées were made shelf stable using both MWS and traditional heat retorting. Retorted chicken and dumplings entrées were also processed in a standard US Army foil lamination. Subsequent accelerated conditions storage and taste panel evaluation at Natick labs indicated preference for the MWS-prepared entrees over the retorted ones.

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Light Barrier for Non-Foil Packaging

Forward

This report comprises an overview of the Objective, Background, Methods, Results, and Conclusions of this contract. These are then followed by seven (7) detailed reports on its specific research activities. Future work is planned to incorporate all findings of this year's research into a better performing all-polymeric barrier material for additional evaluation using traditional and novel food processing technologies.

Special thanks for contributions to this work are due to Joseph Marcy, Ph.D. and Sean O'Keefe, Ph. D. of the Food Science and Technology Department (Virginia Tech, Blacksburg, VA) and Juming Tang, Ph. D, and Galina Mikhaylenko of the Department Of Biological Systems Engineering (Washington State U., Pullman, WA) for their contributions to research reproduced in Annexes here.

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1. Executive Summary

Several goals motivate the US Army Natick Soldier Research, Development, and Engineering Center (NSRDEC) to develop non-foil alternatives for the packaging materials now used to package various field ration items. In doing so, the protection afforded the rations from environmental oxygen, water vapor, and light by foil must be replaced by alternate materials. This study determined that all-plastic laminations can provide oxygen and light barrier at levels measured in field-worn ration packaging, however, they do not reach desired moisture barrier levels. The alternative materials processed well though commercial form-fill-seal packaging and pouch-making equipment without experiencing "stress cracking" commonly noticed with commercial foil laminations. Packages of an entrée item, a dessert bar, and hot-filled cheese sauce are currently in accelerated shelf-life testing at NSRDEC.

2. Objective

The technical objective of this contract is to research and develop "advanced materials/films/coatings for flexible and semi-rigid polymeric containers that provide physical and chemical protection comparable to traditional aluminum foil-based high barrier polymeric materials." for its combat rations, "Meals-ready-to-Eat ("MREs") (NSRDEC, 2007). This report compiles the work done by Printpack Inc. under the subject contract to address this need for both thermoprocessing and novel thermal/nonthermal (i.e. microwave sterilization) processing. Other low water activity foods that do not require thermal processing were also packaged in all-plastic trial material. Specifically, these goals were addressed by the research;

1. To summarize the state of current knowledge concerning the effects of light on food systems in combat rations.
2. To assemble the best available, non-foil, light barrier packaging materials as candidates to replace the current foil lamination.
3. To measure relevant physical properties of the materials assembled in No. 2.
4. To validate the effectiveness of the light barrier from the best of these materials by exposing olive oil and yoghurt packaged in them to light abuse and measuring photodegradation products.
5. To produce the optimum material from No 2, as suggested by Nos. 3 and 4, and use it to package MRE entrée, dessert bar, and hot fill cheese sauce combat rations items.

Subsequent accelerated shelf life testing and taste panel evaluations will compare the food products packaged in No. 5 to identical products packaged in control packaging materials in order to assess progress toward providing the existing three–year shelf life for MREs without foil. Importantly, the entrée items packaged in No.5 were sterilized in the microwave sterilization (MWS) process at Washington State University. This process is in the final stages of validation by the US FDA as a thermal sterilization process, and this research provided confirmation of the process' suitability for pouched products and complex food systems.

3. Background

The cited "physical and chemical protection" comparable to existing combat ration packaging material are for the present time only qualitatively understood. The Army NSRDEC requires three-year shelf life for rations stored at 27°C (80°F) or six months at 38°C (100°F).At present, trained taste panels determine if packaged rations stored at indicated temperatures remain acceptable for warfighter consumption. (Ratto et al, 2006) Empirical determination of the actual oxygen and water vapor barrier of current foil laminations damaged by normal storage and transport abuse indicate these specifications for a packaging material:

- OTR ≤ 0.06 cc/m^2/day
- WVTR ≤ 0.01 g/m^2/day

(DOD Specification "MIL.-PRF-44073F)

Without better quantitative predictors of shelf life protection, this study plan proposed to compare product in all-plastic laminations to identical product in foil laminations using taste panel evaluations. An all-plastic packaging material must protect rations from environmental challenges other than moisture and oxygen, particularly light and aromas. Figure A summarizes the project work plan and indicates previous reports submitted (shaded blocks) to NSRDEC.

In additional to the original 5 goals described above, two other critical ones were identified during project execution:

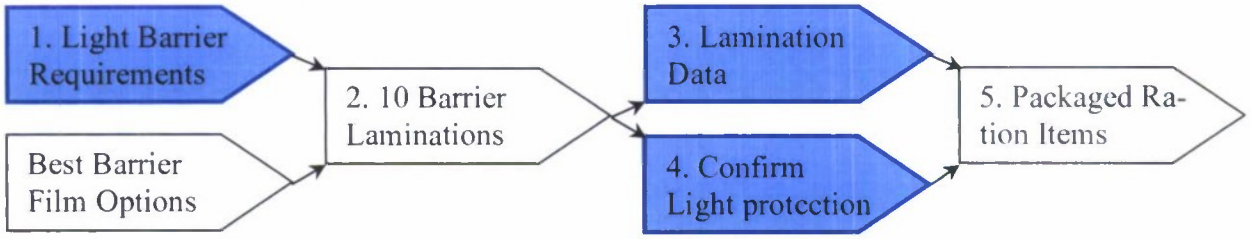
1. Water barrier improvements, compared to neat polyethylene (PE) and polypropylene (PP) films, have been documented with nanocomposites of these resins with multilayered silicates (MLS), e.g. exfoliated clay particles blended into the resins with high aspect ratios. Because this improvement alone is small relative to the water vapor transmission rate specified by the NSRDEC, blending other high-water barrier polyolefins was assessed.
2. The first phase of research identified the need for essentially opaque packaging materials (300-700 nm). Because the industry standard opacifying technique involves blending carbon black into polymers, and such carbon absorbs microwave energy, development of a standard technique for assessing the dielectric properties of thin packaging materials was addressed. The technique will be used to select packaging materials allowing maximum productivity and thermal efficiency of a MWS process

This final report summarizes previous reports addressing all eight goals and incorporates them as annexes here.

4. Methods

1. Light effects on combat rations: Dr. Joseph E. Marcy, department Head, Food Science and Technology, Virginia Tech University, provided a literature survey of the effects of light on the flavor and nutritional quality of various food systems.
2. Best Available, Non-foil, Light Barrier Packaging Materials: The Printpack research team reviewed product literature and research papers to identify available barrier films and resins. Resins were coextruded into multi-functional (sealing and barrier) films to be later laminated to other barrier materials. A pigmented high performance

Figure B: Contract work Plan and Previous Reports



(heat resistance and interlaminar bond strength) adhesive was used to laminate the films and provide light barrier.

3. Properties of films produced in Step 2: Physical, barrier (oxygen, water vapor) and optical properties (UV-Visible) light over the spectrum indicated above) of these laminations were determined. Barrier values for "flat", "5 Gelbo-flexed" and "10 Gelbo-flexed" film samples were determined. Laminations providing the best barrier properties and durability were selected for further evaluation insteps 4 and 5.
4. Light Barrier Effectiveness: Olive oil and full fat yogurt were packaged in control (foil lamination), clear and light barrier materials and then exposed to intense light energy for 96 hours. Solid phase microextraction gas chromatography determined hexanal levels in the samples.
5. Packaged Combat Ration Items in Optimum Structure: MRE Chicken & Dumplings entrée, peanut butter dessert bar, and hot fill cheese items were packaged in a control lamination and an all plastic lamination of 12µ OPET/12µ Al_2O_3-coated OPET/15µ hybrid-coated OPA/75µ polyolefin. The entrées item in foil and all-plastic materials were retorted and a second set of all-plastic packaged entrees were Microwave (MW) Sterilized on the Washington State University (WSU) Pilot line.
6. Nanocomposite Polyolefins for improved WVTR: Previously published research by NSRDEC indicating improved WVTR from cast PP-clay nanocomposite blends was repeated and additional improvements sought by using blends of polynorborene (COC) with PP.
7. Dielectric Properties of Flexible Packaging Materials: An existing technique of WSU to characterize food for optimal processing in its MW sterilization process was adapted for characterizing thin packaging laminations. A defined-geometry resonance cavity allowed measurement of the properties.

5. Results

Individual reports for each of the seven tasks are included as annexes 1-7. Following are summaries of key findings by task

1. Light effects on combat rations: Dr. Marcy's literature survey indicated that the mechanisms of photodegradation for such complex food systems as combat rations dictate essentially complete UV and visible light (300-700 nm) barrier for combat ration packaging.

2. Best Available, Non-foil, Light Barrier Paekaging Materials: Printpack research team reviewed product literature and researeh papers to identify available barrier films and resins. Resins were coextruded into multi-functional (sealing and barrier) films to be later laminated to other barrier materials. The OPET films and pigmented adhesives combined to imparted substantial UV and visible light barrier.

3. Properties of films produeed in Step 2: Physieal, barrier (oxygen, water vapor) and optical properties (UV-Visible light over the speetrum indieated above) of these laminations were determined. Barrier values for flat, "5 Gelbo-flexed" and "10 Gelboflexed" film samples were determined. Two differeni Japanese transparent barrier eoating technologies, Toppan "GL" OPET for retort applieations and Kuraristercoated (hybrid organic and inorganic coating) OPET and OPA delivered the best barrier performance. OTR levels approached and even met the NSRDEC requirements, but the best WVTR found was 5-10 times higher than the target. Laminations providing the best barrier properties and durability were selected for further evaluation insteps 4 and 5.

4. Light Barrier Effeetiveness: Olive oil and full fat yogurt were packaged in control (a foil lamination), clear and light barrier materials and then exposed to intense light energy for 96 hours. Solid phase microextraction gas chromatography determined hexanal levels in the foil and light Barrier materials were statically identical, and both significantly lower than the clear-packaged product

5. Packaged Combat Ration Items in Optimum Structure: MRE Chicken & Dumpling entrée, peanut butter dessert bar, and hot fill eheese items were packaged in a control lamination and an all plastie lamination of 12µ OPET/12µ Al_2O_3-coated OPET/15µ OPA/75µ polyolefin. The entrées item in foil and all-plastic materials were retorted and a seeond set of all-plastie packaged entrees were Microwave Sterilized on the Washington State University Pilot line. Materials all functional well on commercial paekaging maehinery (multi-lane vertical liquid filler for the cheese and horizontal vaeuum thermo-form-fill-seal line for the dessert bars.) Entrée items were hand-packed into pre-formed pouches. In all cases, the plastic packages indicated less flexeraeking than the commereial foil laminations (particularly in seal areas.)

6. Nanocomposite Polyolefins for improved WVTR: the NSRDEC results with PP- nanoelay partieles were reproduced, but signifieant proeessing issues and material brittleness prevent the PP/COC nanoeomposites evaluated here from providing needed WVTR improvements. Multilayered PP/COC coextrusions may offer an alternative for enhanced WVTR.

7. Dieleetrie Properties of Flexible Paekaging Materials: The WSU method was adapted for flexible films by using a preeisely tuned resonance cavity to restrain the film sample while exposed to MW energy. A network analyzer quantified reflected, absorbed and transmitted Microwave energy and computed values for ε' and ε" (dielectric constant and dielectric loss respectively) for the laminations of Task 2 and several other materials. The teehnique was able to detect small differences in these values for the various materials. For example, the nanoelay-modified MxD6 nylon in structure 7 absorbs more energy than the neat MxD6 nylon of structure 6 (higher e'), but actually shows less tendency to convert that energy to heat (lower e"). This suggests the na-

noclay eomposite would introduee inefficieney into the mierowave process; absorbing microwave energy before it can reaeh packaged food, while not inereasing the temperature of the food-package system.

6. References

NSRDEC, 2007; *Broad Agency Announcement "Solicitation Number "07 - 09 Natick BAA"*; Natick, (Ma); 80pp.

Ratto, Jo Ann, J. Lucciarini, C. Thellen, D. Froio, and N. A. D'Souza, 2006, *The reduction of Solid Waste Associated with Military Ration Packaging* , US Army Soldier System Center, Technical Report, Natick (Ma) TR-06/023. 75pp.

Specification "Mil.-PRF-44073F", 4 September 2001; Requirements 3.1.1.2 and 3.1.1.3 using ASTM D3985 and F372 respectively

Effect of Light Exposure on Food Quality

A Condensed Review

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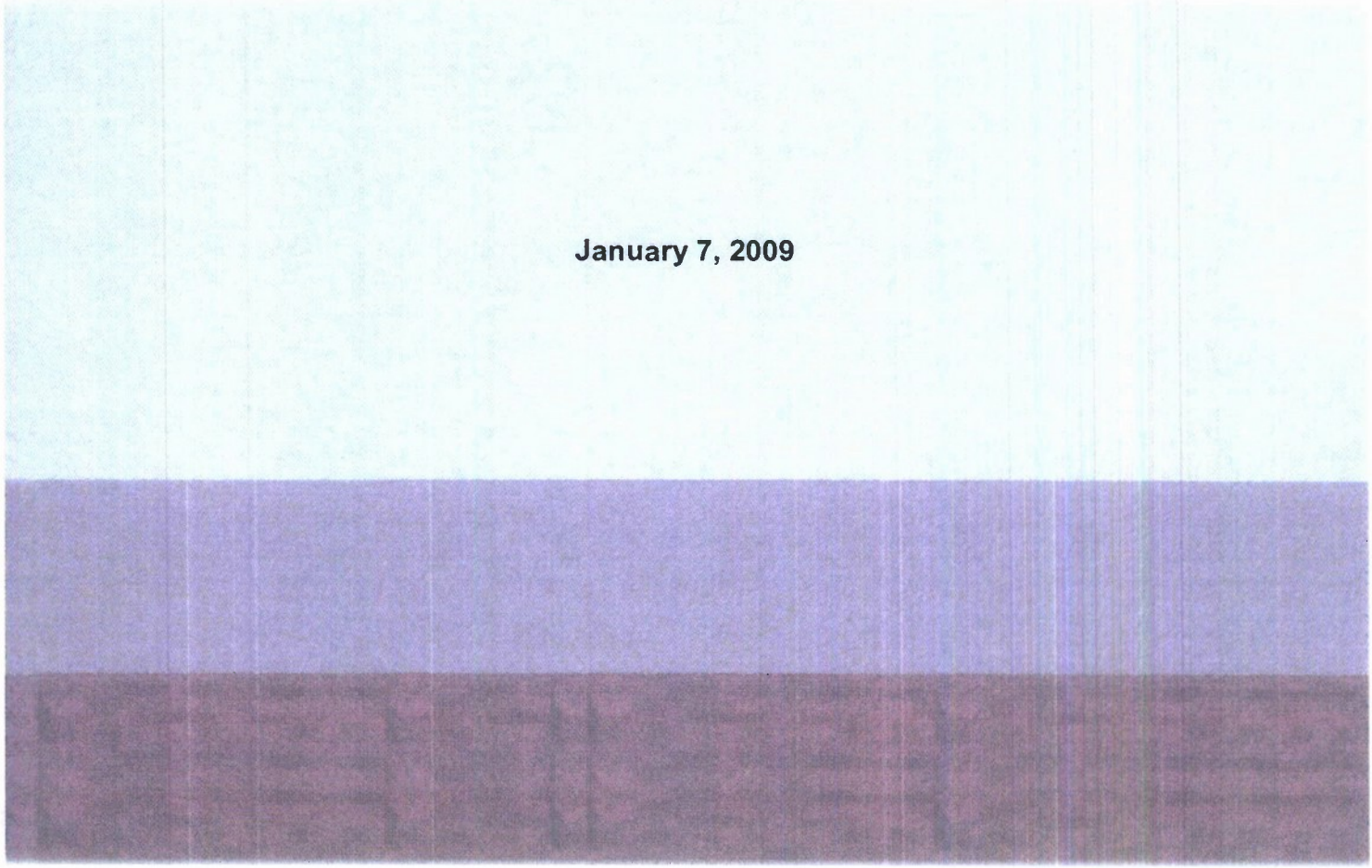
January 7, 2009



Introduction

Sensitivity to natural and artificial light differs greatly from one foodstuff or beverage to the next. Degree of protection offered depends on the absorption characteristics of the material, material thickness, material processing conditions and color of the package. The intensity and spectrum of the light source, the absorption and reflection of the packaging material, and the content and absorption spectra of sensitive components within the food can be used for predicting susceptibility to photooxidative quality deterioration. These factors are often evaluated in order to select the most appropriate packaging material for a given product.

Photooxidation and food quality

Foods exposed to sunlight (natural light) or ambient lighting during production, storage and display can develop a wide variety of adverse effects that cause development of off-flavor compounds and reduce shelf life and nutrient value (Cadwallader and Howard 1998). In opaque foods and beverages, photochemical degradation occurs almost exclusively at the surface because light cannot penetrate very deeply (Bosset et al 1994). Sunlight has been shown to have the strongest oxidation effect, while incandescent light has the weakest (Koo and Kim 1971). Sunlight's emission spectrum is broad and high in energy from both the visible and the UV light range. Duration of light exposure and the intensity and emission spectrum of the light source, as well as the degree of light transmittance of the packaging influences the degree of photooxidation. Photosensitivity of food products is also affected by the content of dissolved or free oxygen and the oxygen permeability of the packaging. The food product's spectrum of light reflection, transmission and absorption are additional factors that contribute to sensitivity (Skibsted 2000; Vassila et al 2002). For many foods, sensory quality can be considerably affected when only a small amount of oxidation occurs due to light exposure (Rosenthal 1992; Jakobsen et al 2005). Trained sensory panelists have been able to detect oxidized flavor in whole and reduced-fat milk packaged in HDPE after 15 to 30 minutes of exposure to 2000 lux light (Chapman et al 2002; Whited et al 2002). Chapman (2002) and Chapman et al (2002) reported that untrained teenagers and adult consumers could detect light-oxidized flavor in milk exposed to 2000 lux fluorescent lighting within 30 to 54 minutes of exposure. Heer et al (1995) found the threshold for detection of light-oxidized flavor to be 2 hours, 40 minutes.

Rate of lipid oxidation is dependent on many factors, but fat composition is an intrinsic component. Food products that are high in unsaturated fatty acids are most susceptible to lipid oxidation. Relative rates of oxidation for stearic, oleic, linoleic and linolenic acids are 1:100:1200:2500 (deMan 1990). Vitamins A, B_2, D, C and riboflavin are particularly affected by light (Bekbolet 1990). The mechanisms of these light-induced reactions have been studied extensively and research into the use of appropriate packaging and enhanced packaging to reduce light-induced changes continues (Tung et al 2001).

Lipid oxidation chemistry

During storage, oxygen-dependent reactions can progress. Oxidation of unsaturated lipids is the primary cause of development of off-flavor compounds and oxidative rancidity, as well as a number of other reactions. Ultimately, primary, secondary and tertiary oxidation products are formed, and these can reduce shelf-life, nutritive value and product safety (deMan 1990). Oxidation reactions occur in two ways. When triplet oxygen (the most abundant and stable form of oxygen) reacts with organic substrates through a free radical mechanism, the reaction is called photolytic auto-oxidation. The second mechanism is through singlet oxygen attack on unsaturated fatty acids (Frankel 1980; Frankel 1991; Yang and Min 1994; Frankel 1998; Min and Boff 2002ab; van Dyck 2007). Interaction with light, sensitizers, and oxygen is responsible for singlet oxygen formation in food, and oxidation of unsaturated lipids with singlet oxygen occurs at a significantly greater rate than with normal triplet oxygen reactions (Bradley and Min 1992; Frankel 1998).

Free radical reactions proceed through three steps. During **initiation**, heat, light or metal abstracts hydrogen from the lipid, producing a free radical. Light is more important than temperature in the formation of radicals during the early stages of oxidation (Kristensen and Skibsted 1999). The peroxyl radical is extremely reactive and will attack points of unsaturation in nearby molecules, leading to **propagation** of the free radical chain reaction. The chain propagation reactions will continue as long as unsaturated lipid or fatty acid molecules are available. **Termination** reactions occur when there is a critical reduction in the amount of unsaturated lipids. Free radicals react with themselves to form stable, non-radical compounds (deMan 1990; Jadhav et al 1996).

Photosensitizers

Natural pigments found in foods that commonly act as photochemical initiators are flavonoids, riboflavin (vitamin B2), chlorophyll, heme and vitamin K. Synthetic food colorants can also act as photosensitizers. Although photooxidation reactions are initiated by light, the compounds being oxidized, such as lipids and proteins, typically do not directly absorb light higher than the wavelength of 220 nm. Photosensitizers do absorb both UV and visible light of specific wavelengths. Then they initiate free radical oxidation reactions through direct contact with the substrate or they produce singlet oxygen and free radicals such as superoxide (Carlsson et al 1976; Aurand et al 1966, 1977; Borle et al 2001; Wold 2006). The presence of a photosensitizer even at the ppm (mg/kg) level can be responsible for production of a highly reactive form of oxygen (Munoz et al 1994).

Light energy must first be absorbed by a chromophore for a photochemical reaction to occur. A chromophore consists of chemical bonds and atom configurations that cause the molecule to absorb light. The specific wavelengths that are absorbed are determined by the particular chromophore in the compound. Specific reactions occur through photosensitization processes in the presence of chromophore impurities such as chlorophyll, porphyrins, myoglobins and phaeophytins (Bekbolet 1990).

Milk contains a number of photosensitizers, most notably riboflavin (Sattar and deMan 1975; Bekbolet 1990; Bradley and Min 1992; Bosset et al 1994; Skibsted 2000; Wold 2006). Riboflavin is one of the most studied photosensitizers and plays a key role in all

problems related to the photosensitivity and photodegradation of milk and dairy produets. It is an orange-yellow vitamin found in high eoneentrations in the whey fraction of milk and it increases thc susceptibility of milk to photooxidation (Sattar et al 1976ab; Bekbolet 1990; Fox and Thayer 1998).

In addition to riboflavin, other compounds ean eontribute to light-induced oxidation. Porphyrins, sueh as hemoglobin, and ehlorins, sueh as chlorophyll, are photosensitizers that have been much less studied than riboflavin. They are found at much lower concentrations than riboflavin but have beeu shown to act very quickly to produce singlet oxygen when they are removed from their native state inside membrane protein. Meat products contain porphyrin pigments and vegetables contain ehlorophyll and chlorophyll derivatives which produce singlet oxygen that make these foods sensitive to photodegradation. Cream and milk have measurable levels of ehlorophyll a and b, but very small amounts of protoporphyrin (Bekbolet 1990; Kessel et al 1993; Wold et al 2005; Wold 2006).

Light Oxidation Flavors

Flavor deterioration of food lipids is caused primarily by volatile lipid oxidation produets that may be present at eoncentrations below 1 ppm. Primary oxidation products are hydroperoxides that are first formed during propagation. Secondary oxidation occurs when hydroperoxides, which are relatively unstable, decompose to form alkanes, alkenes, aldehydes, aleohols, hydroearbons, free fatty aeids, esters, lactones, ketones, furans and cis/trans isomerizations. Thesc components contribute to odor and flavor charaeteristics associated with oxidation, partieularly the earbonyl eompounds sinee they are known to have low thresholds of sensory pereeption. Sensory descriptors sueh as beany, metallic, oily, fishy, painty and rancid are produced by the seeondary products of protein oxidation (Koehar 1996). Formation of tertiary products, sueh as carboxylic acid, from oxidation of aldehydes can also cause odor and flavor problems (Frankel 1980; deMan 1990). Exposure of amino aeids to peroxidizing lipids causes the amino acids to undergo rapid and substantial oxidation. Methionine, eysteine, histidine and lysine have been implicated in this type of oxidation, and compounds formed include imidazole, lactic acid, methionine sulfoxide, hydrogen sulfide, and diaminopentane (Macrae et al 1993; Jadhav et al 1996). In order to estimate the flavor impact of volatile oxidation products, their relative threshold values, along with their eoneentration in a given fat, must be eonsidered (Frankel 1991). Cadwallader and Howard (1998) found dimethyl sulfide (canned corn odor), 2-methylpropanal (dark ehocolate odor), pentanal (sour cut grass odor), hexanal (green eut grass odor), dimethyl disulfide (eooked eabbage odor) and 1-oetene-3-one (earthy, mushroom odor) to be the predominant odor active eompounds in light-oxidized milk. Marsili (1999) reported the same flavor compounds as Cadwallader and Howard (1998) and attributed the development of these flavors to the oxidative breakdown of unsaturated fatty acids, particularly those present in the phospholipids. Van Aardt et al (2005ab) found hexanal (green grass odor), 2-heptanone (eereal, roasted grain odor), n-heptanal (green, fish oil odor), 1-octene-3-ol (mushroom odor), octanal (citrus odor) and nonanal (soapy, floral odor) to be the major aroma-aetive eompounds produced. Friedrich and Aeree (1998) described the aroma-active compounds in milk as green/fish oil, sour grass, sweet,

mushroom, cut-grass, boiled potato, eheesy, pungent, and sulfurous. These odors relate to heptanal, pentanal, heptanol, 1-octene-3-ol, hexanal, dimethyl disulfide, 2, 3-butanedionc, and other sulfur-containing compounds, respectively (Kim and Moor 1996; Cadwallader and Howard 1998).

Lipid oxidation and sensory perception

Hexanal is a common marker used to determine level of lipid oxidation, and it has correlated well with some sensory results (Anderssen and Lingnert 1998; Lennersten and Lingnert 2000). However, other researchers have found a poor correlation between hexanal level and sensory evaluation. Webster (2006) felt that levels of hcxanal were not high enough to explain differenees in light-oxidation flavor in milk with iridescent overwraps. Hedegaard et al (2006) found no differences in hexanal content in milks that had very different sensory characteristics.

As lipids oxidize, they develop a variety of compounds that eontribute off-flavors and off-odors. Lee (2002) stored milk under fluoreseent light and reported that pentanal and hexanal formation oeeurrcd before two hours of exposure and heptanal formed in less than four hours. As fat eontent increased from 0.5% to 3.4%, there was an increase in formation of these eompounds, but not dimethyl sulfide. It has been found that a combination of n-hcxanal, n-heptanal, 2-hexenal and 2-hcptanone produce an oily flavor, and the combination of n-heptanal, n-octanal, n-nonanal, 2-heptanone, 2-heptenal and 2-nonenal produce a tallowy flavor. Pentanal and the C5-C10 alkenals produce a painty flavor in butter (Forss and Stark 1955; Stark and Forss 1962). Goat cheese exposed to fluorescent light for two days developed high levels of 1-heptenol, heptanal, nonanal and 2-decenal which increased goat cheese off-flavor significantly.

Alves et al (2007) found that sensory quality of processed cheese paekaged in polyethylene squeeze tubes deteriorated after four days of storage under fluorescent light (1000 lux) compared to cheese packaged in co-extruded blend of HDPE /LDPE /EVOH (10 days) and polypropylene cups (eight days). Glass-paekaged cheese displayed moderate sensory quality loss after 15 days of storage. Again, these results were attributed to the higher oxygen permeability of the PE tubes.

Webster (2006) found that panelists detected aroma activity exhibited by lower molecular weight eompounds when the milk was exposed to longer visible wavelengths (516 nm, 567 nm, and 610 nm). These compounds produced slight aroma intensities. Higher moleeular weight compounds produeed stronger aroma intensities when milk was exposed to shorter visible (463 nm and 395 nm) and UV wavelengths (200 nm to 400 nm). Exposure to full light resulted in the highest aroma intensities overall. Van Aardt et al (2005a) found similar odor-activc eompounds (hexanal, 2-heptanone, n-heptanal, 1-octene-3-ol, octanal and nonanal) in light-oxidizcd milk treated with antioxidants.

Protein oxidation and sensory perception

Traditionally, the subjeet of oxidation has foeused primarily on lipid oxidation. Howevcr, proteins, pcptides and amino acids are also suseeptible to oxidative changes caused by

free radicals (Davies and Dean 1997, Ostdal et al 2000). Sunlight and fluorescent light can cause photooxidative changes in proteins and amino acids in dairy products, leading to the hydrolysis of peptides. Methionine, tryptophan, cysteine, histidine and tyrosine are particularly photosensitive (Dimick 1976; Bosset et al 1994). Color changes in milk have been attributed to degradation of tyrosine and tryptophan (Toba et al 1980).

Protein oxidation depends not only on the amount of protein available but also on whether it is present as free amino acids, peptides, or proteins. Whey proteins contain many amino acids with sulfur, and they play a key role in protein oxidation (Dimick 1976; Dimick and Kilara 1983).

Proteins, peptides and amino acids undergo free radical oxidation and produce off-flavor compounds more rapidly than lipids; therefore, oxidation of protein and amino acids is responsible for the first off-flavors that appear in milk (Davies and Dean 1997; Ostdal et al 2000). Presence of heat, light, metal, certain food additives, and products of enzymatic and non-enzymatic browning can initiate protein oxidation (Macrae et al 1993). Protein oxidation leads to changes in rheological properties of a food, primarily due to protein cross-linkage, breakdown of protein structure and conformational changes (Davies and Dean 1997; Ostdal et al 2000).

Activated flavor and oxidized flavor are the two categories of off-odor and aroma. Activated flavor arises through oxidation of proteins and results in the burnt feather, burnt protein, scorched, cabbage and mushroom flavor. Oxidized flavor arises from the oxidation of lipids and has been described as wet cardboard, metallic, tallowy or oily flavor (Barnard 1972; Hansen et al 1975).

The essential amino acid methionine is primarily responsible for development of activated flavor in milk (Patton and Josephson 1953; Samuelsson and Harper 1961; Dimick 1976). Dimick (1982) found that sunlight flavor could be detected when methional concentrations were as low as 50 ppb. Dimick and Kilara (1983) determined that sunlight flavor was produced by methionine sulfoxide which is formed from methionine in the presence of light, riboflavin, protein, oxygen.

Light effects on vitamins

Environmental factors that determine rate and extent of light-induced quality deterioration of foods include light source and wavelength intensity, exposure time, and storage temperature. Light sensitivity of a foodstuff depends primarily on its composition, particularly on its content of riboflavin, which acts as a photosensitizer. It is also influenced by the content of sulfur compounds, antioxidants and heavy metals as well as fat composition. Exposure to both ultraviolet (UV) radiation and to the visible light spectrum has been found to cause oxidation of lipids and proteins and to cause degradation of vitamins and colorants in foods (Sattar et al 1977ab; Fanelli et al 1985; Bekbolet 1990; Bosset et al 1995; Skibsted 2000; Borle 2001; Min and Boff 2002b). Generally, visible light is responsible for oxidation during short storage times under low light intensity. With longer storage time and higher light intensity, the autoxidative reactions predominate and short-wave light (especially UV light) becomes the deteriorating factor (Rieblinger et al 1998).

Since vitamins are essential nutrients, their loss by photodegradation decreases the nutritional value of foodstuffs. Reactions of vitamins to light vary greatly according to their absorption spectra. Ascorbic acid, riboflavin, vitamin A, β-carotene, vitamin B_6, vitamin B_{12}, vitamin D, vitamin K, folic acid and tocopherol content can be altered or destroyed when dairy products are exposed to light (Deger and Ashoor 1987; Bosset et al 1994; Marsh et al 1994; Kristensen et al 2000; Borle et al 2001; Saffert et al 2006). Some of these compounds are destroyed by the direct effect of light, and others degrade indirectly by reaction with active oxygen species formed during light-induced oxidation of lipids. Extent of degradation is influenced by the content of the specific product, its position in the matrix, and exposure conditions in relation to the absorption maximum of the specific vitamin (Bosset et al 1994).

Riboflavin (vitamin B_2) degradation

Riboflavin is a highly photosensitive vitamin, and exposure of dairy products to both natural and artificial light causes riboflavin degradation. Riboflavin is found at an average concentration of 1.75 ppm in the whey portion of milk (Dimick 1973). Manicre and Dimick (1975, 1976) determined that 15% and 4% of riboflavin is contained in the casein phase and the fat respectively, in homogenized, pasteurized cow's milk.

The amount of light entering the container is directly proportional to the rate of riboflavin degradation (Sattar et al 1977b; Palanuk et al 1988; Bosset et al 1994). When riboflavin is in its free form and unassociated with milk proteins or fat, the rate of riboflavin degradation increases. Riboflavin absorbs UV light of 250 nm, 270 nm and 370 nm and visible light of 400 nm, 463 nm and 570 nm at neutral pH. Like vitamin A, riboflavin destruction is inversely related to fat content; therefore, as fat decreases, riboflavin loss increases (Manicre and Dimick 1975; Allen and Parks 1979; Gaylord et al 1986). Milk with a lower fat content allows more light to penetrate because light scattering is reduced (Senyk and Shipe 1981).

Riboflavin loss is correlated to an increase in light-oxidized flavor in milk, and it begins degrading before off-flavors are detectable (Allen and Parks 1979). Packaging material, wavelength of light exposure, intensity of light, time of exposure, and temperature all affect the rate of riboflavin degradation (Herreid et al 1952; Dunkley et al 1962; Hedrick and Glass 1975; Sattar and deMan 1975; Deger and Ashoor 1987). Materials that allow penetration of the blue-green bands should not be used for milk and dairy products so that absorption by riboflavin can be avoided.

Gold or yellow pigment, which blocks light from 400-480 nm, partially protects against riboflavin degradation (Luquet et al 1977; Senyk and Shipe 1981; Saffert et al 2006). Fanelli et al (1985) reported that incorporation of 0.3% FD&C Yellow No. 5 into HDPE provided partial protection for vitamin A and riboflavin in milk. Saffert et al (2006) found that whole milk packaged in clear PET bottles lost 33% of its riboflavin content, compared with 11% to 20% loss in milk packaged in white or white and yellow pigmented PET.

Vitamin A

Although vitamin A is stable during heat treatment, it is very sensitive to light and losses of this vitamin occur during storage of products packaged in transparent containers (Ford et al 1969; Thompson and Erdody 1974; Papachristou et al 2006ab; Saffert et al 2006). Vitamin A destruction is dependent on fat content of the product. Amount and rate of degradation increases as fat content decreases because higher-fat milks allow less penetration of light into the milk (Senyk and Shipe 1981; Gaylord et al 1986; Lau et al 1986; deMan 1981, 1990). Vitamin A is removed with the fat during milk processing, necessitating fortification with retinyl palmitate. Added retinyl palmitate has been found to be more susceptible to light destruction than native vitamin A (deMan 1981; Bartholomew and Ogden 1990; Bekbolet 1990). As the level of fortified vitamin A decreases, more vitamin A degradation occurs (Zahar et al 1986). Senyk and Shipe (1981) observed vitamin A-fortified samples of whole, 2% fat, 1% fat, and skim milk packaged in PE containers and exposed to fluorescent light at 200 lux for four hours. Added vitamin A was destroyed at 37%, 44%, 49% and 57% respectively as fat content decreased.

Wavelength of light exposure influences vitamin A retention, and UV light is primarily responsible for its degradation. Wavelengths below 415 nm degrade vitamin A to a greater extent than wavelengths between 415 nm and 455 nm (Sattar et al 1977ab; Fanelli et al 1985; Cladman et al 1998; Mestadagh et al 2005). Hansen and Skibsted (2000) determined that exposure of milk to a wavelength of 366 nm caused more oxidation in a dairy spread than exposure to 405 nm and 436 nm.

Cladman et al (1998) found that green PET provided better protection of vitamin A in milk. Saffert et al (2006) packaged whole milk in 1-liter PET bottles (clear or containing various levels of white or white and yellow pigmentation). Samples were stored under fluorescent lighting (1700 lux). After 10 days, samples stored in clear PET lost 22% of the vitamin A content. Pigmented bottles lost between 0% and 6% of the vitamin A regardless of pigment content. Higher levels of pigmentation did not provide increased protection and are unnecessary for milk stored under commercial conditions. Moyssiadi et al (2004) reported similar results.

Ascorbic acid, folic acid, thiamine (vitamin B_1), cobalamin (vitamin B12), D and E

Oxidation of proteins and amino acids (methionine), as well as destruction of vitamin C and added vitamin A, can be responsible for off-flavor formation (Bekbolet 1990). Thiamine, and vitamins A, D and E are variable in their degradation upon exposure to light.

Oxidation of ascorbic acid to dehydroascorbic acid increases with exposure to light and correlates to light intensity and exposure time (Cakmakci and Turgut 2005). Packaging that contains both oxygen and light barriers are recommended for protection against vitamin C loss. Even then short storage length and low storage temperatures are encouraged (Gliguem and Birlouez-Aragon 2005).

Several researchers have investigated the influence of light on vitamin B_1, or thiamine, with conflicting results. Mohammad et al (1990) reported a thiamine loss in milk of up to 40% after six hours exposure to fluorescent light or sunlight and oxygen. Ferretti et al (1970) found that light-exposed UHT milk stored for 90 days lost 10% of vitamin B_1 compared to samples stored in the dark. However, Ford et al (1969) found no change in

thiamine, biotin and nicotinic acid levels in milk exposed to sunlight. The author did find that sunlight decreased vitamin B_6, B_{12} and folic acid content. Hoppner and Lampi (1985) found no changes in folic acid content of homogenized milk packaged in cardboard, plastic jugs or clear polyethylene bags after 48 hours of fluorescent light exposure (2160 lux).

Cobalamin (vitamin B_{12}) in milk is made up of adenosyl-cobalamin and hydroxy-cobalamin. Adenosyl-cobalamin is known to be light sensitive, but there are contradictory reports regarding the sensitivity of hydroxyl-cobalamin (Ford 1967; Scott et al 1984; Sharma and Lal 1998). Whole milk packaged in 1-liter clear or pigmented (white or white and yellow) PET containers displayed no appreciable loss of vitamin B_{12} after 10 days of exposure to fluorescent lighting at 1700 lux. The vitamin was stable in the white and yellow-pigmented PET (allowing $\approx$ 5% light transmittance) as well as in the clear PET, which allowed more than 50% light transmittance at 450 nm (Saffert et al 2006).

King and Min (1998) stored samples containing various levels of vitamin D and riboflavin in the light or dark for up to eight hours. Oxidation of vitamin D was not observed in samples without riboflavin; however, vitamin D with riboflavin was oxidized under light.

Papaehristou et al (2006a) packaged whole milk in PET with or without UV block or paperboard and stored the samples in the dark for 10 days. Clear PET resulted in 36.6% loss in vitamin E, paperboard stored samples lost 35% and clear PET with UV block lost 26.4% of its vitamin E content. Levels of α-tocopherol have been found to decrease significantly with exposure of oils to light or air (Kiritsakis and Dugan 1985; Psomiadou and Tsimidou 2002ab). Reaction of α-tocopherol with singlet oxygen has resulted in 22% to 35% destruction of the antioxidant when virgin olive oil was exposed to 12100 lux light (Psomiadou and Tsimidou 2002b).

Lighting intensity and display parameters

Many investigators have shown that visible light in the low wavelength range, between 365 nm (black light) and 500 nm (green light), causes a significant increase in light oxidation in milk (Sattar et al 1976ab; Hoskin and Dimick 1979; Bosset et al 1995; Nilson 1999; Hansen and Skibsted 2000; Lennersten and Lingnert 2000; van Aardt et al 2001). Fluorescent light sources are also harmful to products because they produce ultraviolet (UV) light.

Current retail display lighting for foods and lamp selection are neither standardized between stores nor within stores in a particular food chain (Acton 2002). Haisman et al (1992) measured light intensities throughout production (packaging line and cold store), display (three supermarkets), and during transport (shaded daylight). At the dairy plant, light intensities ranged from 220 to 320 lux; at the packaging line, intensities ranged from 80 to 220 lux at the cold store. Light intensities at the supermarkets ranged from 40 to 3480 lux and samples stored in shaded daylights were exposed to 10,000 lux light. Chapman et al (2002) reported that milk was exposed to light intensities between 750 and 6460 lux for 24 hours a day during distribution and marketing. For retail displays, Mottar (1984) concluded that light intensities of approximately 1000 lux were common, but Chapman (2002) and Bosset et al (1994) used 2000 lux as an average with mean exposure time of eight hours.

Webster (2006) found that exposure of milk for seven hours to UV wavelengths between 200 nm and 400 nm and to full light produced the highest levels of hexanal, pentanal and four unidentified volatile compounds. Exposure to 395 nm light resulted in development of these compounds, but not to the extent of 200-400 nm exposure. Photooxidation of milk at these wavelengths probably occurred due to riboflavin sensitization. However, milk exposed to 610 nm light produced pentanal, leading the researcher to conclude that some other sensitizer besides riboflavin is responsible for production of these compounds at this wavelength.

Thron et al (2001) used interference filters to expose sunflower oil spiked with chlorophylls to fluorescent light at specific wavelengths (400 nm, 450 nm, 500 nm, 550 nm, 600 nm and 650 nm). Light in the 400 nm (yellow-green) and 650 nm (blue-green) spectra was found to contribute significantly to chlorophyll sensitization.

Webster (2006) used multi-layers of iridescent film designed to block either a single visible riboflavin excitation wavelength (400 nm, 446 nm or 570 nm) or all three (broad spectrum) from reaching ultra-high temperature (UHT) milk. The broad spectrum wraps did not block the individual riboflavin excitation wavelengths to the extent achieved by the single wavelength block wraps.

Traditional packaging materials

Using colored glass can minimize photooxidation, but there will always be a certain degree of transparency. The color chosen depends on the food product. For example, amber glass is commonly used for beer packaging because it absorbs light in the UV to 500 nm wavelength range. This is the region that is most susceptible to oxidative reactions in beer (Tung et al 2001).

Paper and board packaging are generally used as secondary packaging for transport. This material has limited water protection and can tear or puncture. Paperboard provides additional strength when used as folding cartons and it can be laminated to improve water barrier properties. Laminated multi-layer brick-shaped cartons used in aseptic packaging applications consist of an internal layer of paperboard that lends rigidity and protection to the aluminum foil barrier layer. Additional inner and outer plastic layers provide added protection (Tung et al 2001).

As with glass, plastic materials can be pigmented with various colors to protect against light wavelengths that are most harmful for the specific foodstuff. Incorporation of FDA-approved pigments such as titanium dioxide (TiO_2) into plastic materials increases light scattering and reduces light transmittance, especially at wavelengths shorter than 400 nm (Bradley 1983; Nelson and Cathcart 1984; Lennersten and Lingnert 1998). Light transmission has been found to decrease with increasing levels of added titanium dioxide (deMan 1978).

Carbon black, chalk and talc may also be applied to reduce light transmittance. Carbon black offers maximum protection against UV-VIS radiation (Schroder 1985). And cavitation may be used in the production of polypropylene to add light barrier properties. During the cavitation process, polymers are mixed with small amounts of coloring, which results in an opaque or pearlized film. Lennersten and Lingnert (1998) found that cavitated films reflect more light than non-cavitated films, resulting in reduced light transmittance.

Packaging effects on photooxidation

Light barrier properties of the packaging influence oxidation rate by controlling the intensity and wavelength of light that reaches the food (Hoskin and Dimick 1979; Bekbolet 1990). The primary plastic packaging materials used in the U.S. for refrigerated milk products are high density polyethylene (HDPE) and polyethylene terephthalate (PET) (Anonymous 2002). HDPE is a translucent polymer that transmits up to 62% of light wavelengths between 300 nm and 700 nm. PET is a clear polymer which transmits between 75% and 85% of visible light. It is frequently used for single-serve milk products.

Oxidation flavor is eliminated when milk is packaged in opaque materials (Hoskin and Dimick 1979; Schroder et al 1985; Deger and Ashoor 1987; Hoskin 1988; Haisman et al 1992; Mestagh et al 1992; Boccacci et al 2006). Paperboard or fiberboard packaging is a traditional material that provides excellent protection against light. However, consumers prefer foods such as meat products, confectionery, breads and beverages to be packaged in clear containers so they can see the product. Therefore, even though photooxidation is detrimental to the flavor and nutrition of food, the practice of displaying food in "see through" material continues (Sattar and deMan 1976a; Rosenthal 1992; Cladman et al 1998; Chapman 2002; Young 2002).

Plastic and glass containers allow high light transmittance in both the UV and visible regions of the spectrum, and milk can develop a detectable off-flavor in as little as 12 hours of exposure according to a sensory assessment based on a nine-point hedonic scale and multiple comparison tests (Dimick 1973). Hansen et al (1975) detected sunlight flavor in homogenized milk packaged in glass and plastic after two to four hours of exposure to 40 watt (100 ft candles) cool white fluorescent light. In another study, trained panelists were able to detect off-flavors in milk packaged in clear PET and blue cobalt PET after one to two days of storage under light, while milk packaged in paperboard did not develop detectable off-flavors throughout nine days of testing (Boccacci et al 2006).

Mayonnaise samples stored for 41 days in PET developed high concentrations of hexanal more rapidly than samples stored in polyethylene naphthalate (PEN) and a copolymer composed of PET and PEN. The higher level of hexanal in PET-stored samples was thought to be because PET allows ≈ 40% light transmittance at the wavelength of 365 nm. PEN and PET/PEN only allow ≈ 1% transmission at this wavelength. Levels of hexanal did not differ between the PEN and PET/PEN copolymer after 41 days of storage; however, hexanal concentration did increase in these samples, indicating that visible light affects production of hexanal, but not to the same degree as UV light. Mayonnaise stored in the dark did not increase in hexanal content during 100 days of storage (Lennersten and Lingnert 2000).

Powdered products are very light sensitive because of the large surface area and the high component concentration. Whole milk powder stored for 130 days at room temperature in the daylight was found to contain higher levels of volatile lipid oxidation products than milk powder stored in the dark (Ulberth and Roubicek 1995).

Gvozdenovi et al (2000) packaged powdered orange in paper/polyethylene (Pa/PE), paper/aluminum/polyethylene (Pa/Al/PE), metallized polyester/polyethylene (Pe_{MET}/PE) or in polyester/Al/PE (Pe/Al/PE). Pa/PE, Pa/Al/PE, and Pe/Al/PE allowed no light trans-

mission while the Pe/PE allowed partial light permeability in the UV range. After one year of storage, samples in all types of packaging were darker in color than at the beginning of the study.

Ultra-violet (UV) absorbers can be added to polymer packaging materials such as PET to block UV wavelengths without affecting package clarity. They provide some protection against light oxidized flavor development, but transmission of visible wavelengths is not blocked, and these can damage the product (van Aardt et al 2001). PET with UV block completely blocked light between 300 nm and 350 nm, but transmitted almost all light between 400 nm and 700 nm. Milk packaged in clear PET with UV block (1300 lux light exposure) had significantly less light-oxidation flavor than milk packaged in glass, HDPE and clear PET (van Aardt et al 2001).

UV and visible light wavelength studies

Table 2 summarizes the perceived and absorbed color for wavelength regions 380 nm to 750 nm. The ultraviolet light wavelengths range from 200 nm to 380 nm. UV wavelengths are higher in energy than visible wavelengths, but this part of the emission spectrum can be absorbed by the packaging (glass, polystyrene, polyethylene, and polyethylene terephthalate). Visible light encompasses a wavelength range of 380 nm to 780 nm, and exposure can also lead to product quality deterioration (Bradley 1983; Rosenthal 1992; Borle 2001). Light in the lower wavelength range of the visible spectrum (420 nm to 520 nm; violet-blue) can cause substantial problems, particularly if the product contains riboflavin (Bosset et al 1994, 1995), and heptanal that resulted in a different aroma profile compared to unexposed milk.

Table 2. Wavelength of colors of visible light

Wavelength region (nm)	Perceived color	Absorbed color
380-440	Violet	Yellow-green
440-480	Blue	Yellow
480-490	Green-blue	Orange
490-500	Blue-green	Red
500-560	Green	Purple
560-580	Yellow-green	Violet
580-600	Yellow	Blue
600-620	Orange	Green-blue
620-750	Red	Blue-green

Source: Borle et al 2001

Sattar et al (1976ab) found that wavelengths above 595 nm caused light oxidized flavor in milk. Wold et al (2005, 2006) indicated that exposure to wavelengths between 600 nm and 750 nm affect dairy product quality due to the presence of chlorins and porphyrins

(specifically chlorophyll a and b, protoporphyrin and hematoporphyrin). These compounds are present in most, if not all, dairy products in very small amounts, and these researchers found that they contributed significantly to the oxidation of Norvegia cheese.

Lennersten and Lingnert (2000) observed a rapid increase in hexanal concentration in mayonnaise exposed to blue light with emission peaks at 365 nm, 405 nm, 435 nm and between 410 nm and 470 nm, but this increase was slower when exposed to 365 nm alone. Rate of mayonnaise oxidation was not affected by wavelengths above 470 nm. The lower wavelength caused the highest production of hexanal. Hexanal concentration did not increase when mayonnaise was exposed to 405 nm and 435 nm until the yellowness (b) value had stabilized, indicating that β-carotene had to be completely degraded before oxidation proceeded (Lennersten and Lingnert 2000). Sattar et al (1976ab) similarly found that a decrease in β-carotene corresponded to an increase in peroxide value.

Singh et al (1975) found that yellow pigmented packaging material offered the same protection as paperboard packaging against light oxidation of milk. Hoskin and Dimick (1979) found that yellow polycarbonate containers that blocked light between 380 nm and 480 nm gave intermediate protection against light oxidation flavor in milk when compared to fiberboard and clear glass, HDPE and clear polycarbonate. Milk in the tinted polycarbonate containers had a significantly lower hedonic rating than milk packaged in fiberboard after 24 to 48 hours, while milk packaged in clear containers (polycarbonate, HDPE and glass) had significantly lower hedonic ratings after only 12 hours exposure.

Yellow and clear amorphous polyester/PET lids were compared for light transmission. Yellow lids reduced light transmission to between 0% and 30% from 80% to 90% for the clear lids. Labels on the yellow lids further reduced light transmission to between 0% and 15% (Jakobsen et al 2005).

Van Aardt et al (2001) found that amber pigmented PET, which completely blocks light between 300 nm and 400 nm and partially blocks light between 450 nm and 700 nm, provided almost as much protection against light oxidation as light-protected samples. After three weeks of exposure to light, amber PET-packaged milk contained lower levels of hexanal than milk packaged in PET with UV block, glass, HDPE or clear PET. Milk packaged in PET with a UV block developed less oxidation flavor than glass, clear PET and HDPE after seven days of light exposure. Milk packaged in PET developed lower levels of hexanal and dimethyl disulfide than milk packaged in HDPE.

Webster (2006) found that full light, and light through transparent, violet, blue, and red filters produced the highest amount of oxidation compounds while yellow, green and orange films produced lower amounts of oxidation products.

Light and packaging effects on specific food products

In addition to milk, several products have been the focus of many research studies. These products have very particular reactions to light and deserve to be discussed alone.

Butter

Degree of light-induced oxidation of butter depends on the light source and intensity, exposure time, distance of butter from the light source, and content of β-carotene. Cho-

lesterol oxidation of butter is a reaction that occurs because of singlet oxygen attack on lipids at butter surfaces that are exposed to fluorescent light or sunlight, resulting in development of off-flavors and cholesterol degradation products that have a weak carcinogenic activity (Luby et al 1986ab; Bekbolet 1990). Only aluminum foil and aluminum foil laminates prevent cholesterol oxidation in butter, thereby improving shelf life. Margarine wrap, parchment, wax paper and polyethylene films are not effective light barrier materials (Luby et al 1986b; Emmons et al 1986).

Cholesterol oxidation is more severe when exposed to fluorescent "daylight" or "natural light" than when exposed to warm light. However, such effects have only been observed after very long exposure to light (several weeks at 300 lux), and sensory evaluation determined that all butter samples were unacceptable. Under normal storage conditions (4 °C with packaging protection against light), cholesterol oxidation products, (7α- or 7β-hydroxy cholesterol) were not formed when exposed to light. These compounds develop with extended storage (Nielsen et al 1996b). However, after four days of exposure to UV light at room temperature, detectable amounts of cholesterol oxidation products were formed (Hiesberger and Luf 2000).

Oils

Most cooking oils and salad oils are offered in clear PET packaging because this packaging is lightweight, easier to handle, and inexpensive. Practically all vegetable or seed based oils such as soybean, olive, safflower, cottonseed, and corn contain varying levels of unsaturated linoleates which are very susceptible to light-induced degradation (Andrews 2000; Kiritsakis et al 2002; Min and Boff 2002b). Hydrogenated and unhydrogenated soybean oils display similar patterns of flavor deterioration regardless of container type (Warner and Mounts 1984). Palm oil is more stable than olive oil, but the highest oxidation rate has been observed in sunflower oil (Tawfik and Huyghebaert 1999).

Extra virgin olive oil is considered to be the best olive oil for its organoleptic characteristics, and for its stability and chemical composition. It is practically the only vegetable oil that can be consumed directly in its raw state and it contains important nutritional elements including fatty acids, vitamins and antioxidants (Kiritsakis et al 2002; Caponio et al 205; Mendez and Falque 2007). Shelf-life of sunflower and olive oil under retail display conditions are estimated to be 10.6 and 20.8 months, respectively, as indicated by peroxide value. The shorter shelf life of the sunflower oil has been attributed to the greater rate of oxidation that linoleate undergoes compared to the slower rate for oleate (Kaya et al 1993). Storage of PET-packaged oils in the dark and at low temperatures could prolong shelf-life of oil beyond 24 months (Kueuk and Caner 2005; Kanavouras et al 2006).

Extra virgin olive oils exposed to diffused daylight and artificial light developed high peroxide values in the second or third month of storage and decreased thereafter, while samples stored in the dark attained maximum peroxide values during the sixth month of storage. Samples packaged in PVC demonstrated higher peroxide values compared to those packed in glass. However, none of the samples exceeded the peroxide value of 20 meq O2/kg of olive oil, which is the maximum established by the Council for International Olive Oil in order for an oil to be considered as a virgin oil (Vekiari et al 2007). Capponio et al (2005) found that shelf life of olive oil exposed to diffuse light was shorter

than that of oils kept in the dark, and that after only two months' exposure to light, the oils could no longer be considered extra virgin.

Packaging in brown glass results in significantly improved oil stability compared with glass or clear PET (Warner and Mounts 1984, Kaya et al 1993). Kiritsakis et al (2002) found that colored glass reduces light transmittance in the 670-680 nm range.

Cheeses and color bleaching

Because cheeses are rich in unsaturated fat, they are more prone to oxidation than products that contain primarily saturated fat. Therefore, cheeses containing vegetable oil are more sensitive to oxidation, and high-fat cheeses are more susceptible to oxidative discoloration than low-fat cheeses because they contain more oxidizable substrate (Hong et al 1995ab). Shredded and sliced cheese products have a larger surface area available for light exposure, and they are more susceptible to light-induced oxidation than cheese blocks (Deger and Ashoor 1987; Alves et al 2007; Trobetas et al 2008). Grated cheeses are even more sensitive to light induced deterioration than sliced cheeses (Sieber 2005) detected first because of the high oleic acid content in goat cheese (Kim et al 2003).

Annatto-colored cheese exposed to cool white fluorescent light (3500 lux) developed a measurable pink discoloration (Hong 1995ab). Peterson et al (1999) found that exposure of cheddar cheese to UV light (313 nm and 366 nm) resulted in more definite photobleaching of annatto and β-carotene than exposure to visible light (436 nm). Annatto in a buffer system displayed greater light sensitivity compared with β-carotene and more color bleaching occurred with annatto-colored cheddar cheese than with cheese colored with β-carotene. Vacuum-packaged cheeses stored for 14 days at 8 °C under cool white fluorescent light and covered with burnt orange films had lower thiobarbituric acid values than cheeses covered with clear, sunburst or clear forming films (Hong et al 1995ab).

Beer

Bottled beer undergoes changes in flavor upon exposure to light. A combination of UV and visible light (350-500 nm range) causes degradation of the iso-alpha acids from hops. These acids react with the sulfur-containing amino acids to produce mercaptans that are responsible for the "sunstruck" aroma and flavor in beer (Kamimura and Kaneda 1993). Beer is traditionally packaged in amber or green tinted glass bottles; however, PET packaging variations for bottled beer are emerging. Multilayer polymer construction containing barrier layers that consist of EVOH, MXD-6 nylon, PEN, or that contain oxygen scavengers are being investigated for beer packaging.

Cured meat

Cured meats and cheeses are most often packaged under modified atmospheres and chill-stored. Oxidative quality deterioration leading to development of rancid off-flavors and discoloration can limit shelf-life. Reduction of oxygen and light transmission through the packages during storage is very important.

Cured meats are very susceptible to light-induced discoloration. The nitrosomyoglobin pigment, which is responsible for the cured meat color, dissociates rapidly upon exposure to light in the presence of even small amounts of oxygen, resulting in development of brown, gray and green pigments (Andersen et al 1988, 1990; Andersen and Rasmusen 1992; Bekbolet 1990). During retail display, discoloration of ham can occur very quickly

compared to other deterioration processes (Andersen et al 1988, 1990; Andersen and Rasmussen 1992). Klettner (1984, 1987) evaluated sausage and boiled ham and found that exposure to light caused deterioration in sensory quality. Light source and intensity influenced the rate and amount of color loss. Vacuum packaging using high barrier polymer films can reduce discoloration (Tung 2001).

Oxygen quenchers and antioxidants

Protective mechanisms present in food systems include singlet oxygen quenchers such as α- and β-carotene, ascorbic acid and tocopherols (Kiritsakis and Dugan 1985; Bekbolet 1990; van Dyck 2007). Oxygen quenchers do not prevent singlet oxygen formation, but they may prevent singlet oxygen addition to the allylic double bonds (Carlsson et al 1976; King and Min 1998).

Alpha-tocopherol has been shown to be twice as efficient as ascorbic acid as an oxygen quencher. Alpha- and β-carotene function equally as oxygen quenchers, and tocopherol is not as effective as the carotenes (Kiritsakis and Dugan 1985).

In order to protect flavor, antioxidants are often added to fat-containing foods. Light-exposed milk (10 hours, 1300 lux) with added α-tocopherol (0.025%) and ascorbic acid (0.025%) displayed lower TBARS than both light-protected and light-exposed milk with no added antioxidants. Adding α-tocopherol and ascorbic acid protected against oxidized flavor more effectively than addition of α-tocopherol alone, indicating a synergistic effect between the two compounds (van Aardt et al 2005ab). King and Min (1998) stored samples containing various levels of vitamin D and riboflavin, with and without ascorbic acid or α-tocopherol in the light or dark for up to eight hours. Alpha-tocopherol was found to be more effective than ascorbic acid in quenching singlet oxygen during vitamin D degradation in the presence of riboflavin.

Lycopene is a fat-soluble carotenoid and a precursor of β-carotene. It has twice the antioxidant capacity of β-carotene. Traditionally, tomato sauces have been sold as preserved products packed in glass bottles or metal cans. Today, there is increasing market demand for semi-preserved sauces that are packaged in polymeric materials and displayed under lighting and refrigeration. Photodegradation of lycopene in tomato sauce causes reduction of red color and reduced nutritive value (Baiano et al 2005). Lycopene degradation was about one-fifth that of α- and β-carotene when vegetable juice packaged in glass vials was exposed to 230 foot candles of light at 4°C. After eight days, there was a significant decrease in yellowness that correlated with loss of the carotenoids (Pesek and Warthesen 1987). Baiano et al (2005) packaged semi-preserved tomato sauce in glass, PET, PET with an oxygen scavenger, or polypropylene. Lycopene content decreased faster in PET and PP than in glass or PET containing the oxygen scavenger after four months of storage. Peroxide values were highest in sauces packaged in PET. .

Butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and α-tocopherol have been incorporated into biodegradable and non-biodegradable plastic food packaging. As these compounds migrate into foods such as milk powder, breakfast cereal and crackers, they control development of oxidized flavor (Hoojjat et al 1987; Jadhav et al 1996; van Aardt et al 2007).

Tawfik and Huyghebaert (1999) packaged oils in plastic bottles (PET, PVC, PP or polystyrene) containing BHA and BHT. Although BHA and BHT leached into the oils

from the plastie bottles over 60 days of storage, rate of oxidation was unaffected. Montenegro et al (2007) added gum arabic-microencapsulated lycopene (extracted from fresh tomatoes) to reconstituted skim milk to determine its effieacy as an oxygen quencher. Degradation of vitamins A, and D_3 was reduced by ≈ 45% after exposure to fluorescent light at 8600 lux. Proteetion was attributed to the protein moiety of the gum arabic and to the oxygen quenching effect of the microeneapsulated lycopene.

Conclusions

Integration of results and conclusions that have been reported regarding the effeets of light on foods is very emplieated due to the different detailed methods of reporting experimental design and to the varied methods applied to evaluate the effects. In general, processors may reduce photooxidation by minimizing light exposure and by optimizing barrier properties of the packaging. Storing products in the dark or at least avoiding exposure to visible light (espeeially 400-500 nm) can reduce photoehemieal degradation. The shortest possible duration of light exposure and the lowest possible light intensity, as well as the lowest possible storage temperature, should be used to minimize photooxidation. Processors and retailers should ehoose a mild soft light souree (warm white) as opposed to eold white lighting. Altering light sources and paekaging in nontransparent materials are solutions. Paekaging materials with transparent windows that allow the consumer to view part of the produet is feasible. Choosing an opaque or partially translucent packaging material will protect the vitamin content of the stored food and reduce oxidized flavor development. Choosing a paekaging material which is gas-tight or at least one with low oxygen permeability will reduee photooxidation in stored foods since the presence of oxygen is essential for oxidation reactions to occur. (Borle et al 2001).

The specific sensitivity of the food should be noted when considering packaging type. Maximum packaging protection is not cost effective and sometimes is unnecessary. With regard to dairy products, cream and full-fat milk are less light sensitive than low fat and skim milk due to their greater light scattering properties. Sterilized or UHT products are less photosensitive than raw or minimally pasteurized milks due to their higher content of monosulfide groups. Chocolate or coffee-containing products are less photosensitive There is a tremendously wide variety of paekaging materials available that exhibit different barrier properties, including eardboard, paper, glass, metals, eomposite foils or films (aluminum and plastic), plastic pouches and cups. Generally, metals offer the best proteetion, followed by paper/paperboard, the various plasties and finally glass (Kristofferson et al 1964; Hellerup-Nielsen 1973; Bosset et al 1994). Unbleached paper provides a better light barrier than bleaehed paper, espeeially at shorter wavelengths, because the light-absorbing lignin pigments are removed during the bleaching process (Nilsen 1999).

References:

Complete and detailed references included in full, original report

Annex 2 Best Available, Non-Foil, Light Barrier Packaging Materials

Abstract: The US Army Natick Soldier Research, Development and Engineering Center (NSRDEC) wants to eliminate foil from the packaging materials used in military rations for several reasons. In doing so, the oxygen, water vapor and light barrier functions of foil are lost to the packaging. Laminations of all plastic materials (including various barrier coatings, barrier resins, and composite nanoclay/polymer blends) were evaluated against the functional barrier levels found in foil laminations. Oxygen and light barrier levels approach those of foil materials, but water vapor transmission rates achieved remain 5-10 times higher than provided by foil.

Background: The existing military specification for barrier properties for the retortable MRE pouch is: oxygen transmission rate-- 0.06 cc·day/m^2 and water vapor transmission rate--0.01 gm·day/m^2 (1). The current system provides a minimum shelf life of 3 years at 27°C (80°F) or 6 months at 38°C (100°F). Replacing foil in the MRE pouch addresses several limitations of the current material (2):

- vulnerable to flex cracks
- Subject to pinholes
- Restrictive low temperatures durability
- Limited Airdrop impact durability
- Restricted recycling potential
- Limited/no applicability in novel food sterilization processes
- High visibility of waste in the field

Various plastic materials—in reasonable pouch thicknesses—provide relatively modest barrier protection compared to these foil values. The best available oxygen barrier grades of ethylene vinyl alcohol copolymers (EVOH) in a 25 μ (0.001 inch) thickness can match the foil target at intermediate relative humidities, but far exceed it at the 90% relative humidities experienced in retort processing. Polyolefins provide the highest water vapor barrier levels, but these are well short of the levels specified for MRE pouches.[1]

These barrier shortcomings of basic polymers can be addressed by various coatings and additives[2]. Vacuum aluminum-coated films have many of the same kind of limitations for MRE pouches. As a result, none of these materials were evaluated. Rather, new generation transparent barrier coated films have been evaluated. This includes ceramic (aluminum oxide) and hybrid organic/inorganic coated films (3). Previous work of the NSRDEC with polyolefins using nanoclay additives (4) was repeated in order to enhance water vapor barrier. The objectives of this research include: (i) Determine the oxygen and water vapor barrier possible with functional laminations of best available barrier films; (ii) determine the durability of these barrier levels when stressed with standard flexible film flexing abuse; and, (iii) Assess the ability of the best of these laminations to maintain

[1] Poly-vinylidene chloride (PVdC), has moderate oxygen and water vapor barrier properties, but not adequate to meet the military specification. Because of environmental concerns about halogenated compounds in packaging, no materials containing PVdC were evaluated in this research.

[2] Research for the project did not include "active" barrier technology, such as oxygen scavengers or desiccants. Rather, only "passive" barrier approaches were considered.

the quality of an MRE entrée, and packages combat rations of dessert bars and hot fill cheese sauce. This report will address the first two objectives only.

Methods: Technical data for available commercial films and resins and scientific reports were reviewed to decide what barrier materials to laminate into functional materials for MRE packaging. All components comply with US FDA regulations for food contact materials for high-temperature sterilized foods containing oil or fat (5), and are functionally fit for use in traditional thermal sterilizing and advanced processes.
Table 1 summarizes the basic films used to make the high-barrier laminations. Tables 2 and 3 provide specific detail on the six Printpack coextruded films.

Table 1: Barrier Films used for Laminations

Grade	Supplier	Comment*
Barrier Films/gauge (μ)		
Hybrid ctd. (2s) OPET	Kuraray	Kurarister C/ 12
Hybrid ctd. (2s) BON	Kuraray	Kurarister N/ 15
Al_2O_3 ctd. (1s) OPET	Toppan	GL-ARH/ 12
Foil/ 9	JW	1100 alloy
EVOH coex/ 100	Printpack	N/EVOH/N/t/P
MXD6 coex/ 100	Printpack	N/Mx/N/t/P
nanoMXD6 coex/ 100	Printpack	I/Mx/I/t/P
NanoP Film 1/ 100	Printpack	5Cm/6Cl/27P/62C9
NanoP Film 2/ 100	Printpack	5Cm/8Cl/26P/61C1
NanoP-COC Coex 1/ 100	Printpack	5Cm/6Cl/27P/62C9
Structural Films/gauge (μ)		
Chemically-trtd OPET / 12	SKC	SP93
BON / 15	Honeywell	1500RT
Impact copolymer PP / 75	Tredegar	Extrel 487

***KEY**

BON .....Biaxially oriented nylon
C9.....9 MFR polynorborene
Cm.....Compatibilizer
Cl.....Montmorillonite clay modified with a 4° ammonium salt
EVOH .....32 mol.% ethylene vinyl alcohol copolymer
I .....MxD6 Nylon nanocomposite ("Imperm")
Mx.....MxD6 Nylon
N.....Nylon-6
OPET .....Oriented polyethylene terephthalate
P (CPP).....Polypropylene
t .....Adhesive-tie resin

Table 2: Printpack Barrier Resin Coex Films

Generically	Supplier - Grade	EVOH Coex Layer	MxD6 Coex Layer	nano-MxD6 Coex Layer	Wt. %
nanoMxD6	Nanocor - Imperm 105			1	20.3
Nylon 6	Honeywell - H85QP	1	1		20.3
tie	DuPont-50E662	2	2	2	15.3
Nylon 6	Honeywell - H85QP	3	3		9.0
nanoMxD6	Nanocor - Imperm 105			3	
EVOH	Evalca - F171	4			9.5
MxD6	Mitsubishi - S6011		4	4	9.5
nanoMxD6	Nanocor - Imperm 105			5	9.0
Nylon 6	Honeywell - H85QP	5	5		9.0
tie	DuPont-50E662	6	6	6	15.3
P	Basell-SA861	7	7	7	21.6

Table 3: Printpack Nanocomposite Coex Films

Generically	Supplier/Grade	nano P Film 1 wgt%	nano P Film 2 wgt%	nano P-COC Coex# 1 wgt%
MA-g-PP (MAPP) Compatibilizer	Eastman G-3003	5.0	5.0	5.0
Montmorillonite clay w/ 4° ammonium salt	Pre-dried Cloisite 20A	6.0	8.0	8.0
Random PP Copolymer	Profax SA 861	89	87	26.1
Cyclic Olefin Copolymer MFR=9.2 dg/min	Topas 5013X14	0	0	60.9

#The coex film was 25µ P/50µ blend/25µ P

The nanocomposite blends attempted to surpass the water vapor barrier improvement levels achieved by the NSRDEC work by the additional of cyclic olefin copolymers (polynorborene) to the polypropylene-compatiblizer-modified clay blends of Schirmer (4). Water vapor transmission rates (gm·day/m^2 at 100%RH and 32°C for the three films described in Table 3 were 7.8, 6.8 and 7.6 respectively. These rates are 26% to 38% lower than our blend reproducing the Schirmer blend.

The Table 1 films must be laminated in order to fabricate functional packaging materials. To do so, a Henkel Chemical adhesive system (UR2780-US/UR5891-US) was pigmented to match federal standard FS 16350 (olive-gray). The pigmented system was used for all-plastic laminations and an unpigmented version for the foil control lamination. Table 4 summarizes the ten laminations made (with reference to the material gauges and key of Table 1.) Every "/" in the "structure" column of Table 4 represents a layer with a target 4.9 gm/m^2 (3 lb/3000 ft^2 ream) coating of this adhesive system. The laminations were allowed to cure at 43°C (109°F) for 14 days before further testing.

Table 4: Printpack Barrier Laminations

No.	Structure	Comment
1	OPET/BON/Foil/CPP	Control
2	OPET/Kurarister C/Kurarister N/CPP	Best technical candidate
3	Kurarister C/ PP	Test Kurarister C
4	Kurarister N/ PP	Test Kurarister N
5	GL-ARH/EVOH Coex	Test GLARH for WVTR
6	OPET/MxD6 Coex	Test MxD6 for OTR
7	OPET/nanoMxD6 Coex	Test "Imperm"
8	Kurarister C/ nanoPP-COC Coex1	Test Kurarister C with WVTR plus
9	Kurarister C/ nanoPP-COC Coex2	Test Kurarister C with WVTR plus
10	Kurarister C/ nanoPP-COC Coex3	Test Kurarister C with WVTR plus

A thorough set of physical, visual, and barrier data were developed for each lot of laminations. Attributes and test methods used to measure these are listed in Table 5. UV and visible light absorption (from 300n to 700n), using PerkinElmer Model: Lambda 35 UV/Vis Spectrometer. A data set for each of the ten laminations in included in Appendix A of this report.

Table 5: Data Development for Printpack Laminations

PROPERTY		UNITS	METHOD
Gauge		micron	ASTM F2251
Yield		cm^2 / Kg	ASTM D4321
Basis Weight		gm / m^2	ASTM D646
Gloss @ 45°		%	ASTM D2457
Haze		%	ASTM D1003
Opacity		%	ASTM D589
Tensile Strength	MD	kg / cm^2	ASTM D882
	CMD		
Elongation @ Break	MD	%	ASTM D882
	CMD		
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm width	ASTM D882
	CMD		
Elmendorf Tear	MD	gm	ASTM D689
	CMD		
Coefficient of Friction (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894
	in/in		
Hot Tack Strength		g / 25 mm	ASTM F1921
Heat Seal Strength		g / 25 mm	ASTM F88
WVTR-37.8°C-90% RH	flat	gm/m^2·24 hr	ASTM F1249
WVTR-37.8°C-90% RH	5 gelbo		ASTM F1249 and ASTM F392
WVTR-37.8°C-90% RH	15 gelbo		
OTR-23°C-90% RH	flat	cc/m^2·24 hr	ASTM D3985
OTR-23°C-90% RH	5 gelbo		ASTM D3985 and ASTM F392
OTR-23°C-90% RH	15 gelbo		
OTR-23°C-0% RH	flat	cc/m^2·24 hr	ASTM D3985
OTR-23°C-0% RH	5 gelbo		ASTM D3985 and ASTM F392
OTR-23°C-0% RH	15 gelbo		

Discussion:

Opacity-A previously submitted literature review on the effect of light exposure on food quality concluded that the presence of many sensitive chemical species in combat ration components suggest that complete protection against UV and visible light (i.e. opacity) is advisable. Photosensitizers particularly (e.g. flavonoids, riboflavin --especially for dairy products, chlorophyll, heme compounds, vitamin K, and synthetic food colorants), will degrade the rations in light. Data gathered here indicates that the combination of UV absorption by the plastic films and the visible light absorption by the pigmented adhesive was quite effective in blocking the full range of light. Sample No. 2 in particular with 2 layers of pigmented adhesive transmitted essentially no light over the 200 to 800 nanometer range. Subsequent extended exposure of olive oil and yogurt surrogates to high intensity cool white fluorescent light confirmed the effectiveness of Sample No. 2in protecting the surrogates from photooxidation.

Ma-

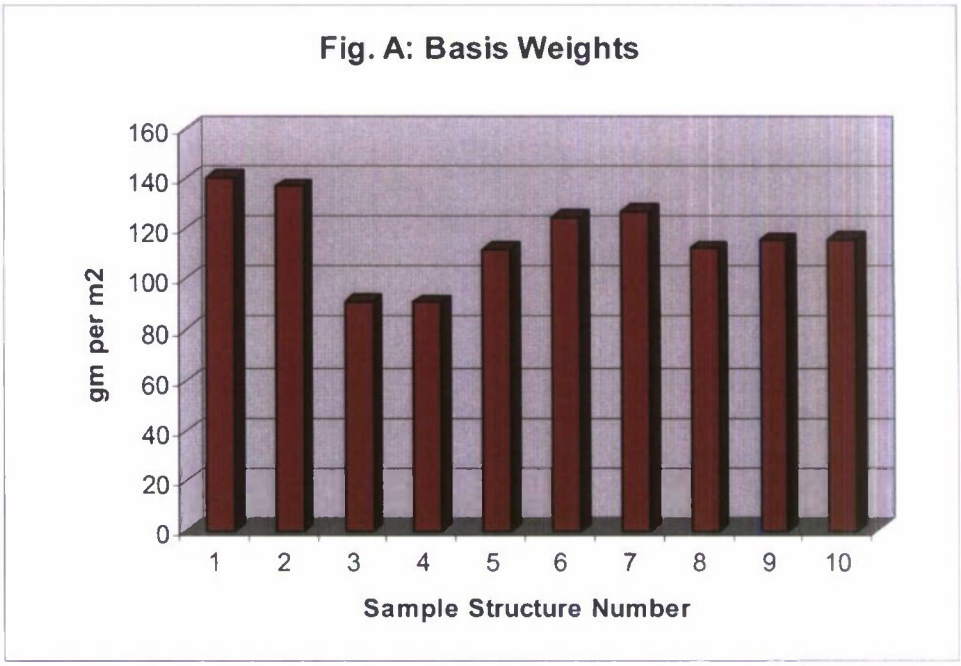


Figure C: Unit weights of sample materials are all less than existing foil lamination

terial Weight-While not a significant part of any one ration item (a 227 gm entrée item requires a 6 to7 gm pouch), the total weight of barrier packaging materials can itself represent a substantial load for a warfighter in the field. Figure A indicates that all of the test structures have a basis weight (weight per unit area) less than the control oil lamination.

Material stiffness- Stiffness (as measured by modulus) affects the efficiency and waste experienced when forming packages and filling them with product. Foil is relatively stiff and so packaging lines optimized to run foil laminations most likely require comparably stiff plastic materials or mechanical adjustments in order to run effectively and efficiently. Figure B provides a measure of the stiffness of the sample materials. The four-ply material (Sample 2) has higher modulus than the control. (Because the sample materials are all multilayer composites, modulus data for them are reported as force per unit sample width rather than force per unit area.). The thicker specialty films laminated to the thin

oriented barrier films (Samples 5-10) approach the stiffness of the control, but the standard 75 μ sealant film laminated to the oriented barrier films have noticeably lower stiffness than the control.

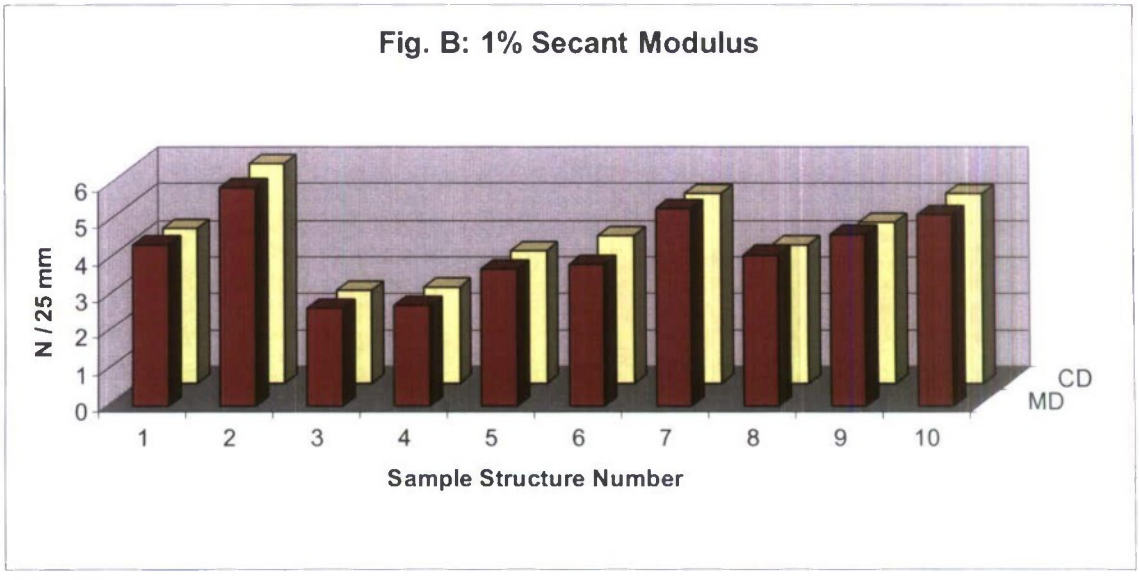


Figure D: The Stiffness of sample materials is similar to existing foil lamination

Water Vapor Barrier- Achieving the WVTR of the standard military ration foil lamination appears to be the most demanding challenge for the nonfoil replacements. Figure C indicates that only Sample No. 5 has WVTR that is less than a factor of 10 greater than the existing specification. This is a lamination of a retort-grade AL_2O_3 1-side coated OPET. It shows relatively good maintenance of the low WVTR even with 10 Gelbo flexes. The brittleness of the COC-PP nanocomposite materials is apparent in the significant loss of WVTR after 10 Gelbo flexes.

Dry Oxygen Barrier- As seen in Figure D, the lamination with retort-grade AL_2O_3 1-side coated OPET (Sample No. 5) demonstrates good OTR at 0% RH, even when flexed. Sample 1 which uses OPET and OBON grades of the barrier coated Kurarister film in a 4-ply lamination also provides excellent dry OTR. The worst performer in this test (Samples No. 6) made use of MxD6 nylon as its primary oxygen barrier material. This polymer is characterized as having less OTR moisture scnitivty that EVOH, but apparently the olefin and barrier coating in the other laminations protected the EVOH from moisture effects. At higher retort times and temperatures, this relative ranking may well change.

Conclusions:

This variety of laminations fabricated with barrier coated films and barrier and nanocomposite resin coex films indicates that state-of-the –art coated films have overcome much of their previous abuse resistance weaknesses. The data collected here indicates that Sample No.2 and a varition of it, with the GL-grade OPET replacing the Kurarister OPET, will be evaluted for further use in the shelf life tests. Further results with the nanocomposite polymers will hep guide future lamination evaluation.

Figure C: WVTRs of samples higher than foil material

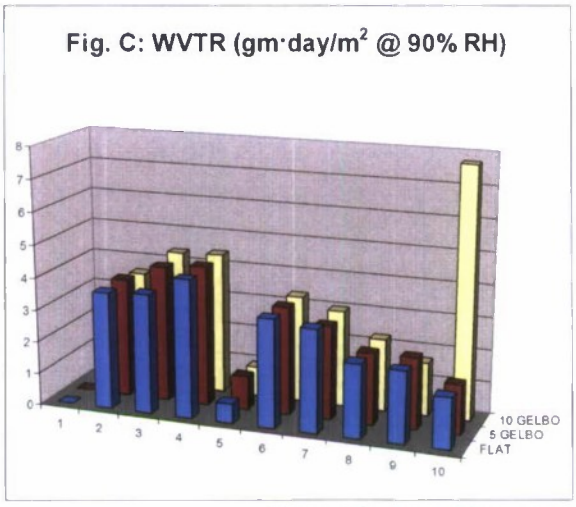


Figure D: Dry OTRs of samples match Foil Lamination

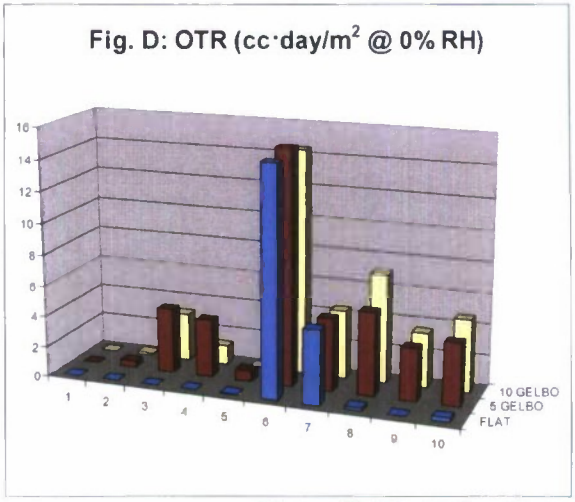
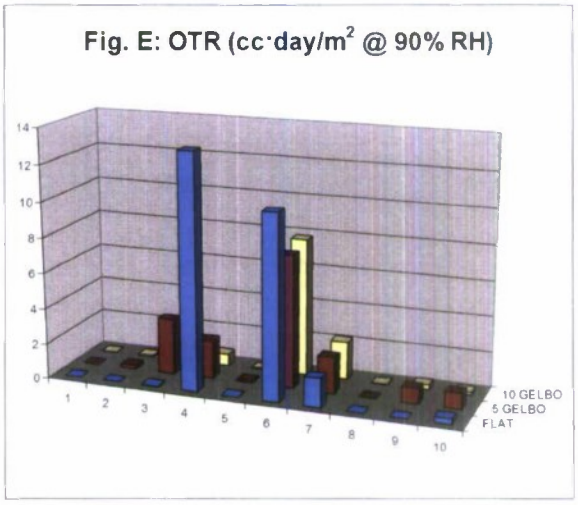


Figure E: Wet OTRs of samples match Foil Lamination



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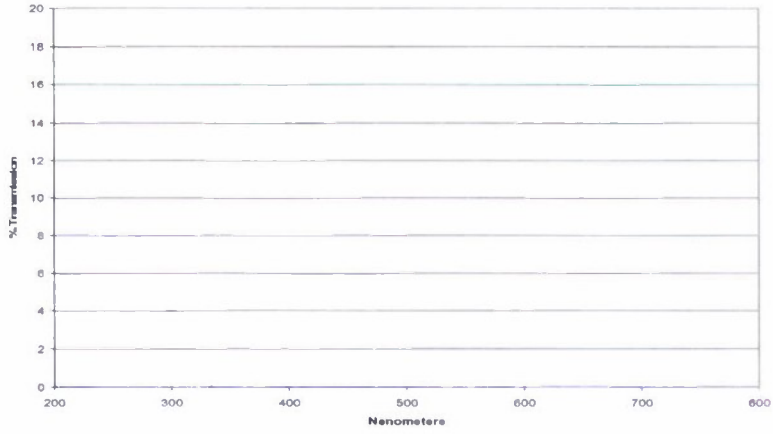
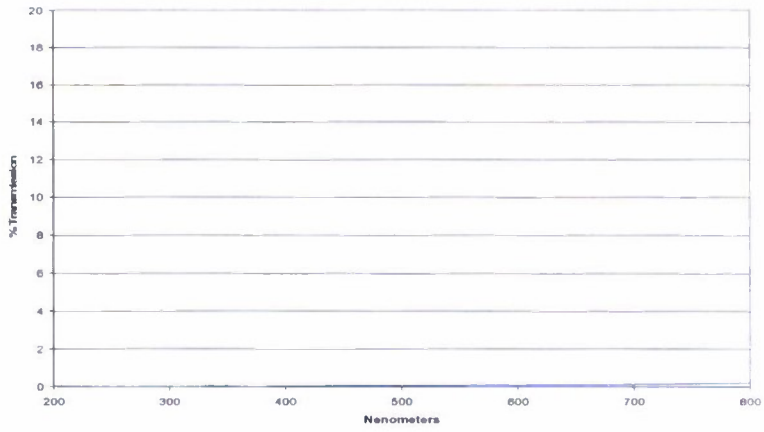
3. Nakamae, Masato, 2009, *Adhesive Composition*, US Patent Application No. 2009/54579
4. Schirmer, Sarah; J. Ratto, D. Froio, C. Thellen, J. Lucciarini, 2008; Nanocomposite Polypropylene Film For Food Packaging Applications: Proceedings of the Annual Technical Conference, Society of Plastics Engineers: Newtown, CT USA
5. Chapter 21 Code of federal Regulations; Part 176.170(c); *Condition of Use A and Food Type III*

Annex 3: Properties of Films Produced in Task 2

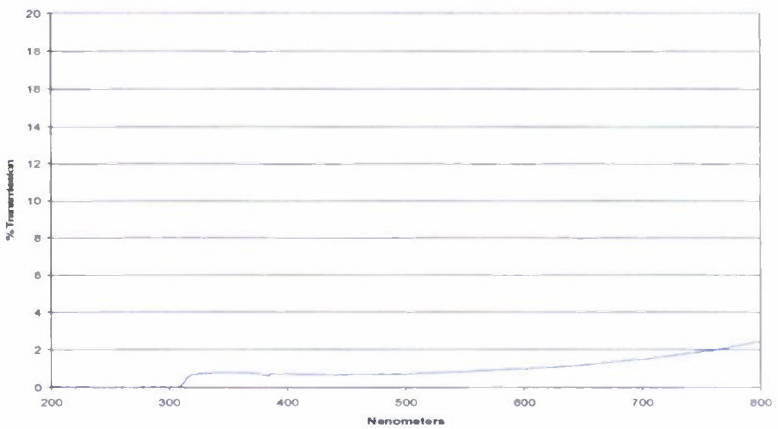
STRUCTURE: 12 µ PET/adh/15 µ BON/adh/9 µ Foil/adh/76 µ CPP				
Structure No. 1				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	125.2
Yield		cm^2 / Kg	ASTM D4321	71271.5
Basis Weight		gm / m^2	ASTM D646	140.3
Gloss @ 45°		%	ASTM D2457	100
Haze		%	ASTM D1003	100
Opacity		%	ASTM D589	99.8
Tensile Strength	MD	kg / 25 mm	ASTM D882	20.2
	CMD			19.7
Elongation @ Break	MD	%	ASTM D882	132.6
	CMD			127.4
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	4.4
	CMD			4.2
Elmendorf Tear (notched)	MD	gm	ASTM D689	173
	CMD			179
COF (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.31
	in/in			0.44
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	1106
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	11803
WVTR-37.8°C-90RH	flat	gm·day/m^2	ASTM F1249	<0.005
WVTR-37.8°C-90RH	5 gelbo		ASTM F1249/	<0.005
WVTR-37.8°C-90RH	10 gelbo		ASTM F392	<0.005
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	<0.005
OTR-23°C-90% RH	5 gelbo		ASTM D3985/	<0.005
OTR-23°C-90% RH	10 gelbo		ASTM F392	0.006
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	<0.005
OTR-23°C-0% RH	5 gelbo		ASTM D3985/	<0.005
OTR-23°C-0% RH	10 gelbo		ASTM F392	0.008



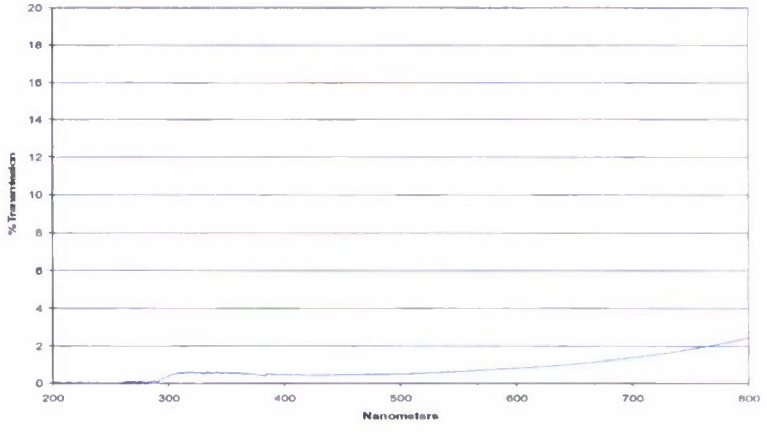
STRUCTURE:	12 µ PET/adh/12 µ KurPET/adh/15 µ KurBON/adh/ 76 µ CPP			
Structure No. 2				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	132.1
Yield		cm^2 / Kg	ASTM D4321	73220.0
Basis Weight		gm / m^2	ASTM D646	136.5
Gloss @ 45°		%	ASTM D2457	78
Haze		%	ASTM D1003	100
Opacity		%	ASTM D589	96.2
Tensile Strength	MD	kg / 25 mm	ASTM D882	22.1
	CMD			23.6
Elongation @ Break	MD	%	ASTM D882	123.5
	CMD			108.3
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	5.9
	CMD			6.0
Elmendorf Tear (notched)	MD	gm	ASTM D689	170
	CMD			179
COF (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.29
	in/in			0.41
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	885
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	6604
WVTR-37.8°C-90RH	flat	gm·day/m^2	ASTM F1249	3.640
WVTR-37.8°C-90RH	5 gelbo		ASTM F1249/	3.700
WVTR-37.8°C-90RH	10 gelbo		ASTM F392	3.560
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	<0.005
OTR-23°C-90% RH	5 gelbo		ASTM D3985/	0.200
OTR-23°C-90% RH	10 gelbo		ASTM F392	0.087
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	<0.005
OTR-23°C-0% RH	5 gelbo		ASTM D3985/	0.406
OTR-23°C-0% RH	10 gelbo		ASTM F392	0.160



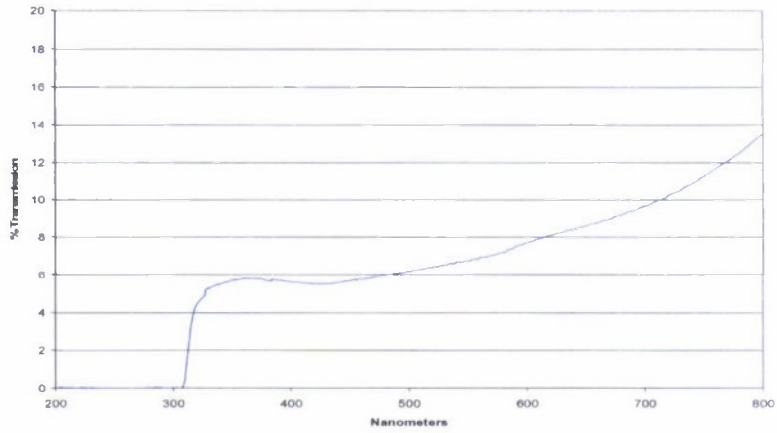
STRUCTURE:	12 µ Kur-PET/adh/ 76 µ CPP			
Structure No. 3				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	94.0
Yield		cm^2 / Kg	ASTM D4321	109915.3
Basis Weight		gm / m^2	ASTM D646	91.0
Gloss @ 45°		%	ASTM D2457	54
Haze		%	ASTM D1003	100
Opacity		%	ASTM D589	60.5
Tensile Strength	MD	kg / 25 mm	ASTM D882	9.9
	CMD			7.8
Elongation @ Break	MD	%	ASTM D882	127.1
	CMD			141.0
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	2.6
	CMD			2.5
Elmendorf Tear (notched)	MD	gm	ASTM D689	128
	CMD			169
COF (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.22
	in/in			0.43
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	1167
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	8187
WVTR-37.8°C-90RH	flat	gm·day/m^2	ASTM F1249	3.720
WVTR-37.8°C-90RH	5 gelbo		ASTM F1249/	4.230
WVTR-37.8°C-90RH	10 gelbo		ASTM F392	4.350
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	0.047
OTR-23°C-90% RH	5 gelbo		ASTM D3985/	3.150
OTR-23°C-90% RH	10 gelbo		ASTM F392	1.870
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	0.012
OTR-23°C-0% RH	5 gelbo		ASTM D3985/	4.205
OTR-23°C-0% RH	10 gelbo		ASTM F392	3.100



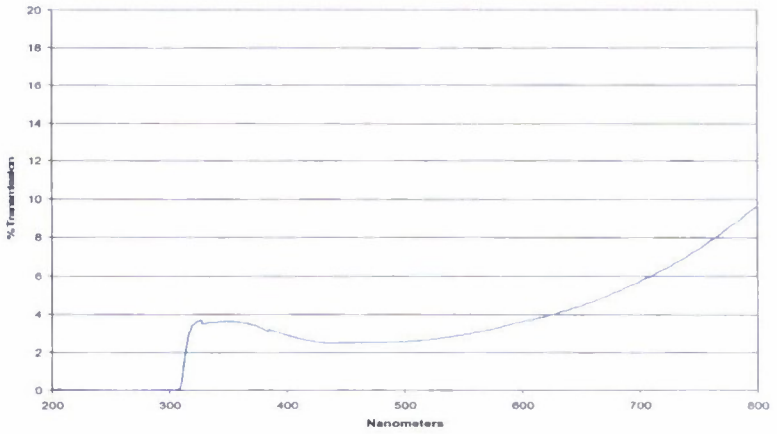
STRUCTURE:	15 µ Kur-BON/ adh/ 76 µ CPP			
Structure No. 4				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	97.3
Yield		cm^2 / Kg	ASTM D4321	110100.2
Basis Weight		gm / m^2	ASTM D646	90.8
Gloss @ 45°		%	ASTM D2457	56
Haze		%	ASTM D1003	100
Opacity		%	ASTM D589	63.8
Tensile Strength	MD	kg / 25 mm	ASTM D882	10.2
	CMD			8.1
Elongation @ Break	MD	%	ASTM D882	127.1
	CMD			141.0
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	2.7
	CMD			2.6
Elmendorf Tear (notched)	MD	gm	ASTM D689	153
	CMD			144
COF (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.33
	in/in			0.38
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	1374
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	8120
WVTR-37.8°C-90RH	flat	gm·day/m^2	ASTM F1249	4.290
WVTR-37.8°C-90RH	5 gelbo		ASTM F1249/	4.350
WVTR-37.8°C-90RH	10 gelbo		ASTM F392	4.410
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	13.218
OTR-23°C-90% RH	5 gelbo		ASTM D3985/	2.170
OTR-23°C-90% RH	10 gelbo		ASTM F392	0.688
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	0.025
OTR-23°C-0% RH	5 gelbo		ASTM D3985/	3.760
OTR-23°C-0% RH	10 gelbo		ASTM F392	1.255



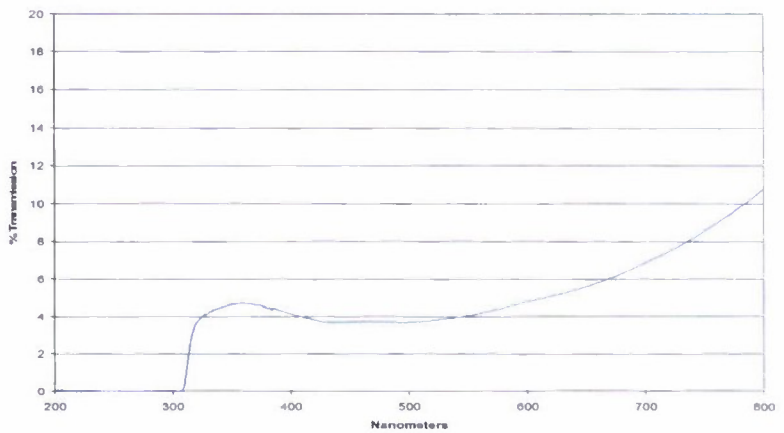
STRUCTURE:	12 µ AlOx PET/ adh/ 101 µ EVOH Coex			
Structure No. 5				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	108.2
Yield		cm^2 / Kg	ASTM D4321	89562.2
Basis Weight		gm / m^2	ASTM D646	111.6
Gloss @ 45°		%	ASTM D2457	77
Haze		%	ASTM D1003	90
Opacity		%	ASTM D589	59.3
Tensile Strength	MD	kg / 25 mm	ASTM D882	11.6
	CMD			10.8
Elongation @ Break	MD	%	ASTM D882	76.7
	CMD			60.7
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	3.7
	CMD			3.6
Elmendorf Tear (notched)	MD	gm	ASTM D689	124
	CMD			156
COF (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.27
	in/in			0.24
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	452
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	9969
WVTR-37.8°C-90RH	flat	gm·day/m^2	ASTM F1249	0.6
WVTR-37.8°C-90RH	5 gelbo		ASTM F1249/	1.0
WVTR-37.8°C-90RH	10 gelbo		ASTM F392	0.9
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	0.017
OTR-23°C-90% RH	5 gelbo		ASTM D3985/	0.116
OTR-23°C-90% RH	10 gelbo		ASTM F392	0.069
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	0.046
OTR-23°C-0% RH	5 gelbo		ASTM D3985/	0.695
OTR-23°C-0% RH	10 gelbo		ASTM F392	0.088



STRUCTURE:	12 µ PET/ adh/ 101 µ MXD6 Coex			
Structure No. 6				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	119.6
Yield		cm^2 / Kg	ASTM D4321	80516.4
Basis Weight		gm / m^2	ASTM D646	124.2
Gloss @ 45°		%	ASTM D2457	78
Haze		%	ASTM D1003	93
Opacity		%	ASTM D589	60.9
Tensile Strength	MD	kg / 25 mm	ASTM D882	11.9
	CMD			11.9
Elongation @ Break	MD	%	ASTM D882	60.0
	CMD			42.8
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	3.8
	CMD			4.0
Elmendorf Tear (notched)	MD	gm	ASTM D689	230
	CMD			352
COF (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.29
	in/in			0.18
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	470
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	11028
WVTR-37.8°C-90RH	flat	gm·day/m^2	ASTM F1249	3.4
WVTR-37.8°C-90RH	5 gelbo		ASTM F1249/	3.4
WVTR-37.8°C-90RH	10 gelbo		ASTM F392	3.3
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	10.350
OTR-23°C-90% RH	5 gelbo		ASTM D3985/	7.495
OTR-23°C-90% RH	10 gelbo		ASTM F392	7.800
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	14.700
OTR-23°C-0% RH	5 gelbo		ASTM D3985/	15.100
OTR-23°C-0% RH	10 gelbo		ASTM F392	14.500

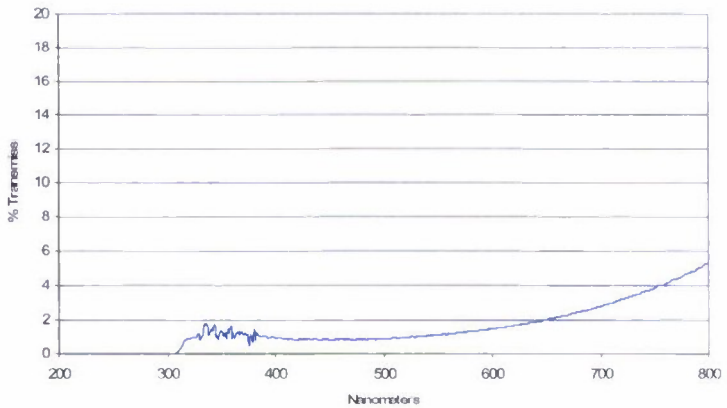


STRUCTURE:	12 µ PET/ adh/ 101 µ nano-MXD6-EVOH Coex			
Structure No. 7				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	122.7
Yield		cm^2 / Kg	ASTM D4321	78767.0
Basis Weight		gm / m^2	ASTM D646	126.9
Gloss @ 45°		%	ASTM D2457	78
Haze		%	ASTM D1003	91
Opacity		%	ASTM D589	59.1
Tensile Strength	MD	kg / 25 mm	ASTM D882	14.2
	CMD			17.1
Elongation @ Break	MD	%	ASTM D882	47.8
	CMD			10.7
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	5.4
	CMD			5.2
Elmendorf Tear (notched)	MD	gm	ASTM D689	99
	CMD			124
COF (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.36
	in/in			0.26
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	482
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	6389
WVTR-37.8°C-90RH	flat	gm·day/m^2	ASTM F1249	3.2
WVTR-37.8°C-90RH	5 gelbo		ASTM F1249/	2.9
WVTR-37.8°C-90RH	10 gelbo		ASTM F392	3.0
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	1.605
OTR-23°C-90% RH	5 gelbo		ASTM D3985/	2.045
OTR-23°C-90% RH	10 gelbo		ASTM F392	2.175
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	4.795
OTR-23°C-0% RH	5 gelbo		ASTM D3985/	4.715
OTR-23°C-0% RH	10 gelbo		ASTM F392	4.425



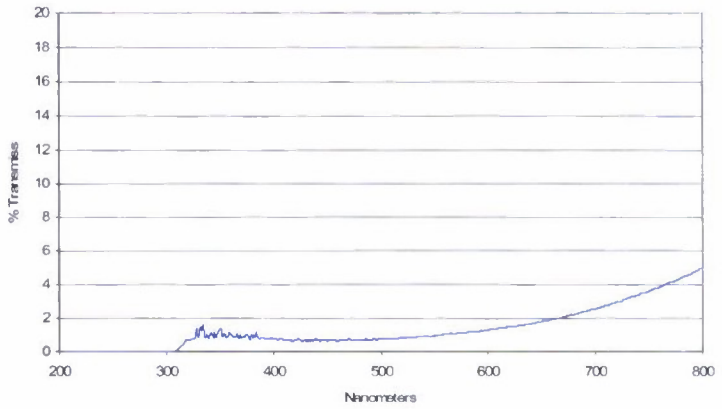
STRUCTURE:	12 µ KurPET/101 µ 6% nano P film			
Structure No. 8				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	113.8
Yield		cm^2 / Kg	ASTM D4321	18345.9
Basis Weight		gm / m^2	ASTM D646	112.1
Gloss @ 45°		%	ASTM D2457	53
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	70.0
Tensile Strength	MD	kg / 25 mm	ASTM D882	6.9
	CMD			6.4
Elongation @ Break	MD	%	ASTM D882	583.0
	CMD			554.0
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	4.1
	CMD			3.7
Elmendorf Tear (notched)	MD	gm	ASTM D689	80
	CMD			106
COF (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.14
	in/in			0.43
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	398
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	5297
WVTR-37.8°C-90RH	flat	gm·day/m^2	ASTM F1249	2.305
WVTR-37.8°C-90RH	5 gelbo		ASTM F1249/	2.200
WVTR-37.8°C-90RH	10 gelbo		ASTM F392	2.252
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	<0.005
OTR-23°C-90% RH	5 gelbo		ASTM D3985/	0.006
OTR-23°C-90% RH	10 gelbo		ASTM F392	0.012
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	0.195
OTR-23°C-0% RH	5 gelbo		ASTM D3985/	5.405
OTR-23°C-0% RH	10 gelbo		ASTM F392	7.081

Structure No. 8



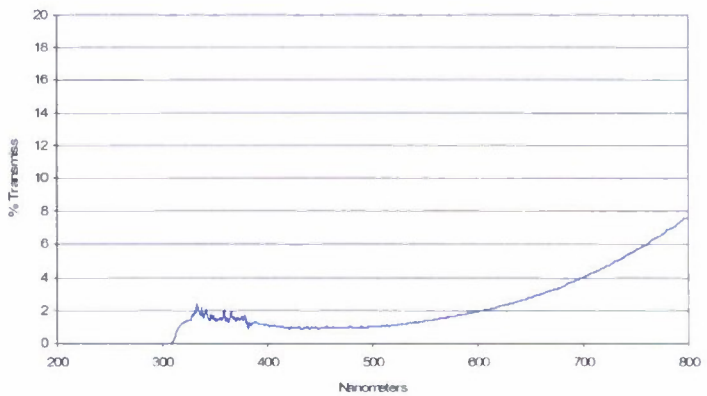
STRUCTURE:	12 µ KurPET/101 µ 8% nano P film			
Structure No. 9				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	119.9
Yield		cm^2 / Kg	ASTM D4321	17830.8
Basis Weight		gm / m^2	ASTM D646	115.4
Gloss @ 45°		%	ASTM D2457	51
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	71.0
Tensile Strength	MD	kg / 25 mm	ASTM D882	7.0
	CMD			6.4
Elongation @ Break	MD	%	ASTM D882	588.0
	CMD			550.0
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	4.7
	CMD			4.4
Elmendorf Tear (notched)	MD	gm	ASTM D689	80
	CMD			99
COF (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.18
	in/in			0.38
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	335
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	6593
WVTR-37.8°C-90RH	flat	gm·day/m^2	ASTM F1249	2.248
WVTR-37.8°C-90RH	5 gelbo		ASTM F1249/	2.228
WVTR-37.8°C-90RH	10 gelbo		ASTM F392	1.665
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	0.006
OTR-23°C-90% RH	5 gelbo		ASTM D3985/	0.845
OTR-23°C-90% RH	10 gelbo		ASTM F392	0.260
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	0.026
OTR-23°C-0% RH	5 gelbo		ASTM D3985/	3.399
OTR-23°C-0% RH	10 gelbo		ASTM F392	3.578

Structure No. 9



STRUCTURE:	12 µ KurPET/101 µ P-8% nano P&COC-P coex			
Structure No. 10				
PROPERTY		**UNITS**	**METHOD**	**VALUE**
Gauge		micron	ASTM F2251	106.4
Yield		cm^2 / Kg	ASTM D4321	17754.8
Basis Weight		gm / m^2	ASTM D646	115.9
Gloss @ 45°		%	ASTM D2457	51
Haze		%	ASTM D1003	n/a
Opacity		%	ASTM D589	66.0
Tensile Strength	MD	kg / 25 mm	ASTM D882	13.8
	CMD			11.3
Elongation @ Break	MD	%	ASTM D882	15.0
	CMD			7.0
Young's Modulus (1% Secant Modulus)	MD	N / 25 mm	ASTM D882	5.2
	CMD			5.1
Elmendorf Tear (notched)	MD	gm	ASTM D689	48
	CMD			74
COF (kinetic)	out/out	gm vertical/gm lateral	ASTM D1894	0.14
	in/in			0.46
Hot Tack Strength	300 F	gm / 25 mm	ASTM F1921	421
Heat Seal Strength	320 F	gm / 25 mm	ASTM F88	464
WVTR-37.8°C-90RH	flat	gm·day/m^2	ASTM F1249	1.618
WVTR-37.8°C-90RH	5 gelbo		ASTM F1249/	1.556
WVTR-37.8°C-90RH	10 gelbo		ASTM F392	7.736
OTR-23°C-90% RH	flat	cc·day/m^2	ASTM D3985	0.317
OTR-23°C-90% RH	5 gelbo		ASTM D3985/	0.890
OTR-23°C-90% RH	10 gelbo		ASTM F392	0.149
OTR-23°C-0% RH	flat	cc·day/m^2	ASTM D3985	0.252
OTR-23°C-0% RH	5 gelbo		ASTM D3985/	4.053
OTR-23°C-0% RH	10 gelbo		ASTM F392	4.711

Structure No. 10



Annex 4 Light Barrier Effectiveness

Photooxidation Effects in Olive Oil and Yoghurt Packaged in Clear, Non Foil Barrier, And Foil Barrier Packaging

Final Report From

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Department of Food Science and Technology
Virginia Tech
Blacksburg
VA 24061

To

Tom Dunn
Product Development Director
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Atlanta GA 30339

4/30/09

Experiments were conducted to determine the effect of package film type (clear, non-foil barrier and foil barrier) on photo oxidation in olive oil and yoghurt, as assessed by using headspace analysis of hexanal concentrations using gas chromatography mass spectrometry with solid phase microextraction.

The hexanal concentration in the olive oil stored in foil and non-foil barrier film packages were not significantly different from one another ($p>0.05$) whereas the hexanal concentration in the clear film package was significantly higher than the barrier packages.

Similar results were obtained for yoghurt (clear film was highest and barrier films were not significantly different from one another). The results show that photo oxidation of olive oil and yoghurt packaged in non-foil barrier film is not different from those packaged in foil barrier film.

Experimental

Experimental packaging films were obtained from Tom Dunn and were marked as:

1. Clear film: 48 ga Al_2O_3 OPET/60 ga BON/2 mil PP
2. Foil barrier film: OPET/BON/foil/CPP
3. Non-foil barrier film: OPET/ctdPET/ctdBON/CPP

The films will be called clear, foil barrier and non foil barrier in the text below. Pouches of dimensions 2" x 10" and sealed on three sides were prepared from the linear film using the sealing element in a Koeh X200 Vacuum packager. The sealing time was adjusted for proper sealing with the individual films in preliminary experiments. Extra Virgin Olive Oil (Kroger Brand) and full fat yoghurt (Dannon all natural plain) were obtained from Kroger Supermarkets. Pouches were filled with 10ml of yoghurt or olive oil, minimal headspace left, and the pouches sealed. Triplicate samples were prepared.

Samples were irradiated at 5 °C with2050 lux light from Sylvania cool white fluorescent lights for 96 hours. Packages were rotated in the irradiation chamber daily to ensure equal irradiation. Preliminary experiments indicated that there was a significant increase in headspace hexanal in olive oil irradiated in glass containers under these conditions.

After irradiation, exactly 4g of yoghurt or olive oil were transferred to 15ml headspace vials and the vials capped using Teflon-lined silicone septa. A Hewlett-Packard model 5890 gas chromatograph was used for volatile analysis. The detector was a HP MSD Mass Spectrometer and a Leap Technologies solid phase microextraction (SPME) autosampler (CTS Analytics) was used for SPME analysis. A divinylbenzene/carboxen/ polydimethylsiloxane fiber (50/30μm) for autosampler was used to extract headspace volatiles. Incubation temperature for headspace analysis was 40 °C for 30 minutes with agitation. The gas chromatograph column was a 30m x 0.25mm i.d., 0.25 μ film, HP-5 5% diphenyl 95% dimethylpolysiloxane bonded capillary column operated using helium

carrier gas at 25 cm/sec linear velocity. The oven program was 50°C to 225°C at 5°C/min

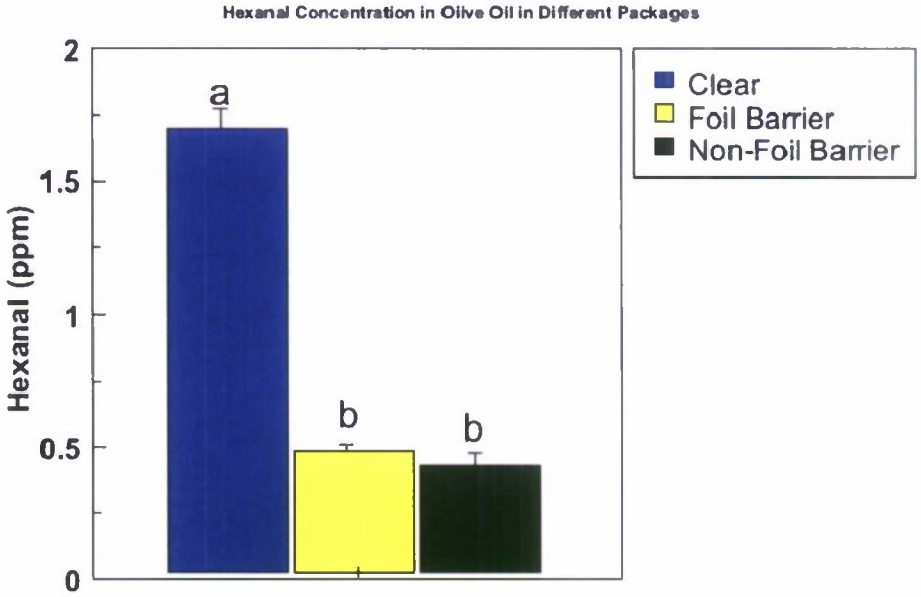
Solutions of hexanal were prepared in distilled water and were analyzed at the same time for retention time identification and quantitative analysis. The hexanal peak in chromatograms was identified by comparing retention times and mass spectra with authentic standard. Hexanal peak areas from samples were obtained and compared to the standard curve prepared in distilled water.

Means were compared by using One Way Analysis of Variance using Microsoft Excel version XP. Mean separations were conducted using the least significant difference test when the ANOVA was significant (protected LSD). Means were considered significantly different at $p<0.05$.

Results and Discussion

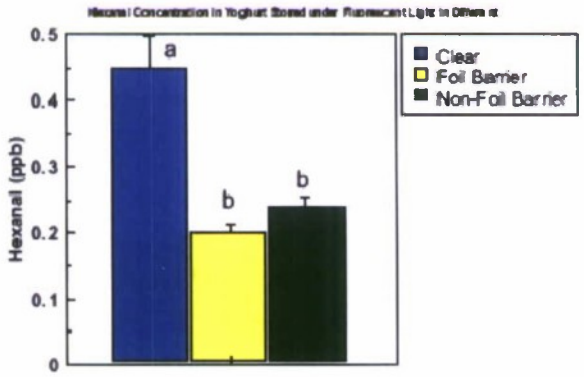
Preliminary studies showed that a storage time for 4 days at 5°C with 2050 lux irradiation was sufficient to cause significant photo oxidation in olive oil stored in glass. The hexanal contents of olive oil irradiated in the three packages are shown in Figure 1 (raw data appear in Appendix I). The hexanal content of olive oil irradiated in non-foil barrier packages was not significantly different from the barrier packages ($p>0.05$). Some hexanal was observed in oil irradiated in the barrier packages. This is expected, as there is a background oxidation in commercial oil samples that can be detected by using headspace hexanal analysis.

Figure 1. Hexanal content of olive oil after irradiation in clear, foil-barrier and nonfoil barrier films for 96 hours at 5°C and 2050 lux fluorescent light. Bars represent means and SEM; bars with different letters are significantly different ($p<0.05$).



The hexanal coneentrations that were observed in yoghurt subjeeted to fluoreseent light irradiation were similar in trend to what was noted for olive oil, but concentrations were mueh lower. The samples stored and irradiated in the two barrier paekages again were not different from one another ($p>0.05$), but were both significantly lower than the samples stored in the clear film ($p<0.05$).

Figure 2. Hexanal content of plain, full fat yoghurt after irradiation in clear, foil barrier and non-foil barrier films for 96 hours at 5°C and 2050 lux fluorescent light. Bars represent means and SEM; bars with different letters are significantly different ($p<0.05$).



The difference in hexanal levels between the two samples is probably attributable to the differenees in the sample matrix (hexanal is more soluble in oil than in aqueous foods) and the native oxidation present in the two oils. The relatively high saturation in dairy fats makes them less prone to oxidation during storage.

The photo proteetive effeets of non foil barrier and foil barrier films were not different from one another under the experimental conditions examined.

Annex 5 Packaged Combat Rations in Optimum Structure

SUMMARY OF THE CHICKEN DUMPLINGS PRODUCT PREPARATION AND PROCESSING AT WASHINGTON STATE UNIVERSITY

2009

Submitted to Natick Army Center and Printpack Inc
By
Galina Mikhaylenko

On behalf of microwave heating group

Department of Biological Systems Engineering
Washington State University
October 26, 2009

This report summarizes work performed for the production of chicken dumplings in pouches for the WSU-Printpack subcontract with Natick for the shelf life sensory evaluation. Report outlines product development, filling, sealing procedures, and processing conditions for this product.

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Appendixes:

Appendix 3. Microbiological report for spore testing in microwave processed pouches (Silliker, CA)

Appendix 4. Microbiological report for Listeria and Salmonella testing in microwave processed pouches (Silliker, CA)

Appendix 5. Statistical sampling reference for microbiological testing.

1. Product development

Chicken dumplings product was developed using specifications outlined in the part of the document PCR-C-067 provided by Tom Yang (Natick Army Center) as a guideline. The major difficulties for the recipe development were sauce syneresis and overall product consistency. The syneresis of the product occurred at two stages: during processing (cook loss by the muscle during HTST cooking resulting in excess of watery phase) and then after about 2 weeks of storage at 4°C (most likely due to starch retrogradation). Combinations of various modified starches and gums were tested to improve the final product consistency. The following strategy was employed to minimize the syneresis: 1) screening of the sauce formulations in kinetic test cells after heating in oil bath at 121°C; 2) screening of sauce formulations cooked at 121 °C after a week of storage at 4°C; 3) screening of the sauce formulations that pass stage 1 and 2 in a whole product; 4) adjusting the concentration of the stabilizers as needed (Fig 1.1.). A large "product development" 100 ml capacity test cell was designed, manufactured and used for these preliminary trials. Development of this cell significantly contributed to the speeding up the process of product development allowing judging overall flavor, texture and composition of the product on a small scale in a relatively short time (Fig 1.1.c and d).

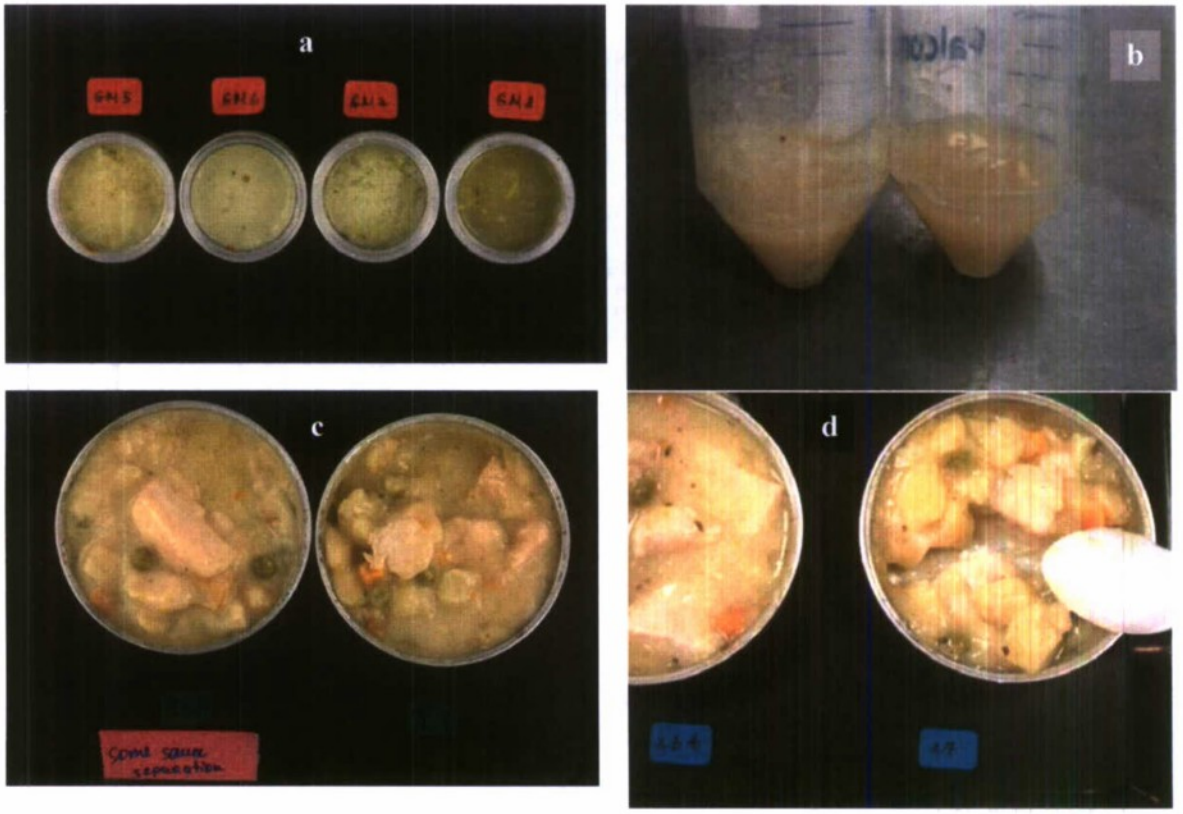


Fig.1.1. Stages of product development: a) screening of sauce formulations heated in hermitically sealed kinetic test cells with oil bath at 121°C; b) observation of sauce separation after one week of storage at 4°C; c) screening the formulations that pass stage 1 and 2 in a whole product combination; d) improving formulation and sensory attributes of pre-screened formulations.

The product with two different types of dumplings was sent to Natick in June 2009 for preliminary evaluation. Type 1 dumplings were pre-cooked Spatzle dumplings (Maggie, Germany) and type 2 dumplings were frozen dumplings (Marzetti Frozen Pasta, Inc.). Although, the differences between the products were not statistically significant, the overall preference was given to the type 1 dumplings. The larger size of type 2 dumplings was a desirable characteristic; however, the negative comments about its flavor resulted in exclusion of this product from further testing. In addition, from the observation of the processed product, the recipe with type 1 dumplings had more appealing appearance after processing.

The finalized recipe for chicken dumplings contained 39% sauce, 42% chicken, 12.3% dumplings and 6.7% peas and carrots mix. Sauce ingredients were: chicken stock, cream, modified starches, olive oil, xanthan gum, and spices.

Table 1. Pouch weight distribution over three batches dispensed using All-Fill.

Pouch #	Weight of the pouches (g)		
(As consecutively dispensed in batch)	Batch 1 (Day 1)	Batch 2 (Day 1)	Batch 3 (Day 2)
1	232.4	231.7	226.9
10	232.2	233.2	231.6
20	233.9	229.2	225.8*
30	228.3	225.7*	
Average batch wgt g	231.7 ± 2.4	230 ± 3.9	229.3 ± 3.3

*Product ran out.

During actual production run, the weights of the dispensed product were checked after start of the dispensing and at least once throughout the dispensing of the batch. The weights were always above 227 g.

The pouches with less then 227 g were diverted from the general sealing line to be used as fillers for the pouches containing Ellab temperature sensors. Pouches containing Ellab sensors were only used in microwave sterilization system.

2.2. Packaging procedures

2.2.1. Packaging material

Alternative size 8 oz plastic laminate pouches were produced by Printpack Inc (Atlanta, GA).

The composition of a plastic laminate is as follows:

12µ Oriented Polyester
9 gm/m² pigmented adhesive
12µ Oriented Polyester with Al_2O_3 vapor-deposited coating
.4 gm/ m² adhesive
15µ Oriented Polyamide with hybrid organic/inorganic coating
9 gm/ m² pigmented adhesive
75 µ PP sealant

The composition of an aluminum laminate is as follows:

12µ Oriented Polyester
9 gm/ m² adhesive
15µ Oriented Polyamide
9 gm/ m² adhesive
9µ 1100 Foil
9 gm/ m² adhesive
75 µ cast PP sealant

2.2.2. Packaging equipment and parameters

Custom modifications were implemented to the existing Mini-Pack Torre pouch sealer to improve the seal strength. The sealed pouches were tested in the custom made internal pressure/burst apparatus and complied with the requirements to withstand the pressure of 20 PSIG for 30 sec.

The residual air in the sealed pouches was reduced to not exceed 20 cc. The sealer vacuum settings were adjusted to meet specifications. The pouches were vacuum sealed with atmospheric air, no gas flush was used. The amount of residual air was measured by direct measurement of the volume of displaced water in the cylinder that captured air bubbles coming from the tear opened pouch. The average residual air measured in 10 pouches dispensed in preliminary product trials (three batches) during week of July 27-31 was 12 ± 5 cc. Residual air was checked for a randomly selected pouch for each day of pouch production. The residual air amount was 12 ± 4 cc.

3. Preparation of the chicken dumplings product

3.1. Preparation of Pilot Plant processing facilities

The Pilot Plant processing facilities and equipment were prepared according to GMP for food handling facilities (Fig. 3.1). The ingredients, the filled and sealed pouches were kept on ice at all times. The All-Fill filler was disassembled, cleaned and sanitized after each product preparation batch. The weights of the portions dispensed using All-Fill were checked after each cleaning of the filler.

Pouch seals were visually inspected after sealing. Any defective seals were rejected (only a few pouches were rejected out of 750 produced). A small piece of an autoclave tape was placed on the corner of the pouch to serve as indicator of the processed or unprocessed product.

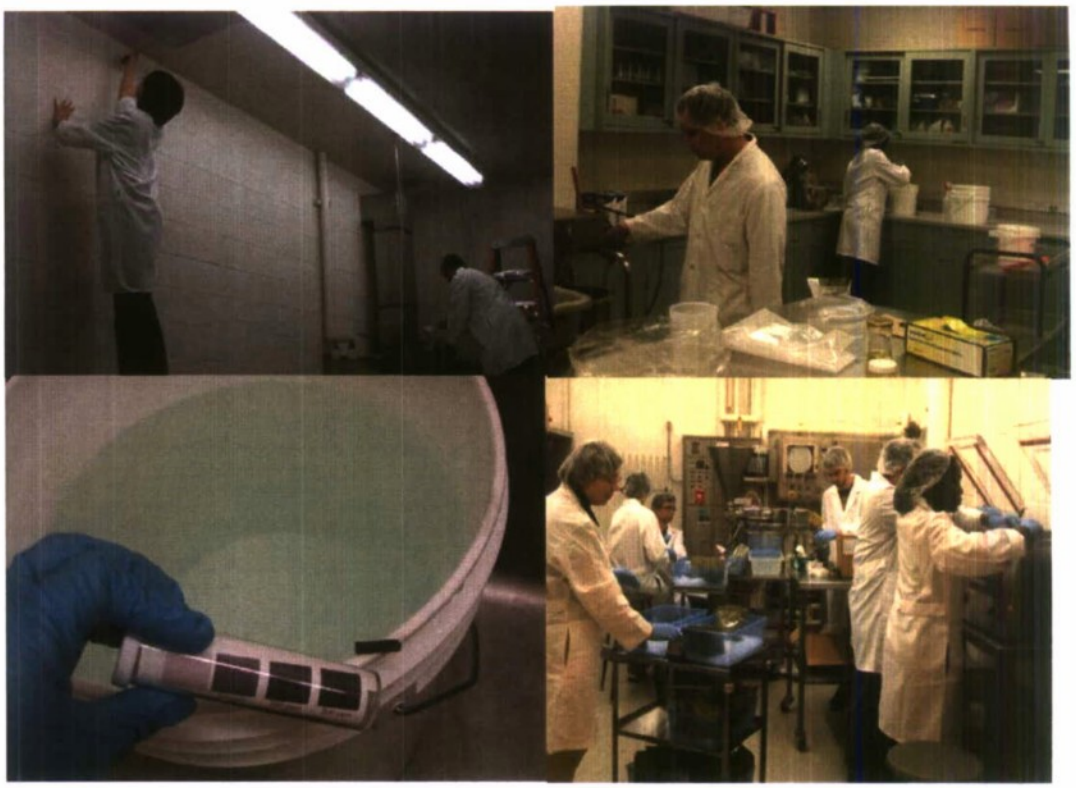


Fig. 3.1. Preparation of WSU facilities for the chicken dumplings product processing.

3.2. Preparation of product in pouches

Total of 750 chicken dumplings pouches were filled and sealed at WSU facility (Fig. 3.2)

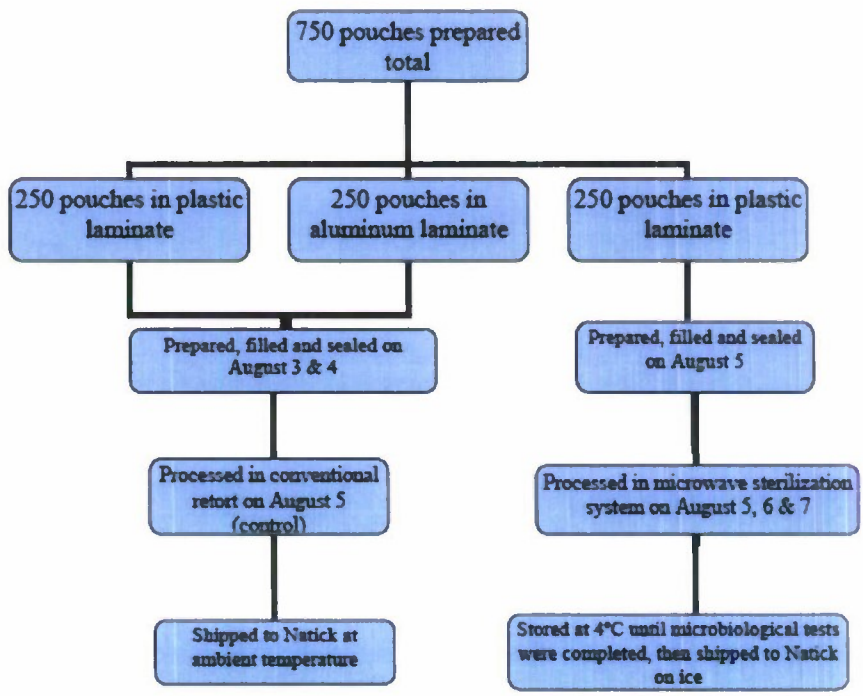


Fig. 3.2. Schematic of product preparation, processing and shipping for the chicken dumplings produced at WSU (August 2009).

500 pouches were prepared for conventional retort processing at Seattle retort facility (as a control for this experiment) on August 3 and 4. Out of 500 pouches 250 were plastic laminate and 250 were aluminum laminate. These 500 pouches were packed on ice and sent by overnight refrigerated truck to Seattle processing facility to be retorted on August 5-6. Processed product was labeled with a stick-on labels provided by WSU and shipped to Natick at ambient temperature.

250 remaining pouches were prepared, filled and sealed for processing in WSU microwave sterilization system on August 5. The sealed pouches were stored at 4°C prior to processing (Fig. 3.3). Pouches were processed in WSU microwave system on August 5-7. All pouches were placed in the cold room at 4°C immediately after processing, stored until microbiological tests were completed, then shipped to Natick on ice.

Fig. 3.3. Sealed product in cold storage (4°C) prior to processing.

4. Processing of the chicken dumplings product

4.1. Cold spot detection and processing schedule development

Procedures for heating pattern and cold spot determination and development of the processing schedule were described in the earlier quarterly report to Natick Army center (Appendix 1).

4.2. Processing of chicken dumplings using microwave sterilization system

250 samples were processed in microwave sterilization system using previously developed schedule (Fig. 4.1)

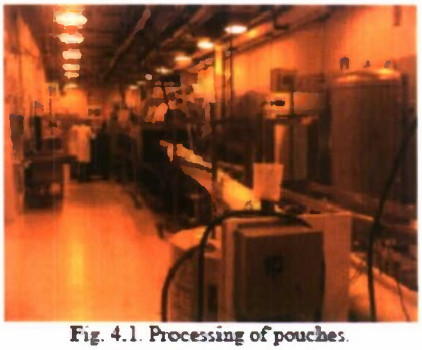


Fig. 4.1. Processing of pouches.

Each microwave processing run contained 42 pouches. 3 pouches in each run contained Ellab sensors for food temperature history recording. A sample of temperature profiles during the MW processing is shown in Fig. 4.2.

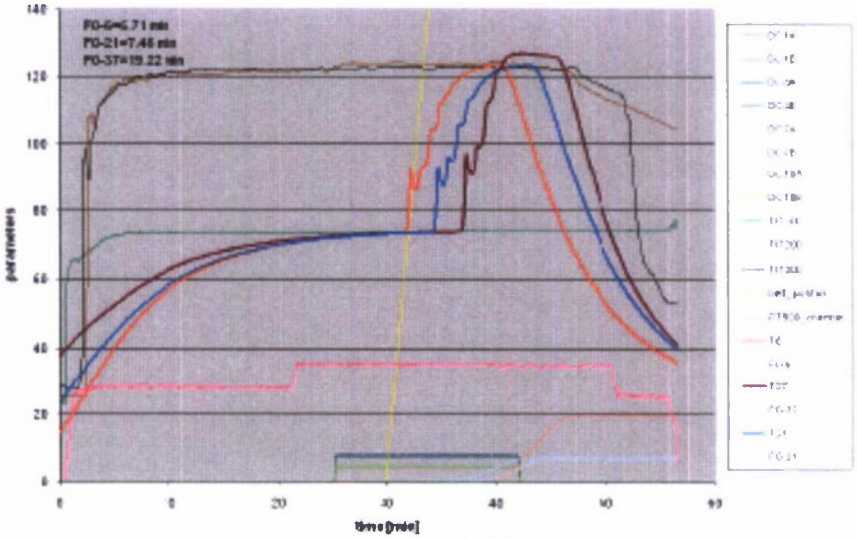


Fig. 4.2. A sample of temperature profiles during MW processing of pouches (Test 2 - Aug. 5, 2009)

The F_0 values observed during MW processing of chicken dumplings pouches are summarized in Table 2.

Table 2. F_0 values for MW processed chicken dumplings.

Run #	Run date	Pouch # w/ Ellab sensor	IT (°C) before processing	F_0 (min after cooling
1	Aug. 05, 2009 Test 2	6-21-37	4.5-4.8-4.8	6.71-7.46-19.22
2	Aug. 05, 2009 Test 3	6-21-37	11.0-13.6-13.1	11.4-17.0-12.15
3	Aug. 06, 2009 Test 1	6-21-37	6.9-6.8-7.3	9.24-15.98-16.91
4	Aug. 06, 2009 Test 2	6-21-37	7.9-9.5-9.4	7.95-19.57-10.28
5	Aug. 06, 2009 Test 3	6-21-37	8.6-11.7-7.4	9.06-15.62-12.59
6	Aug. 06, 2009 Test 4	6-21-37	9.1-10.6-10.3	5.77-11.56-26.42
7	Aug. 07, 2009 Test 1	6-21-37	9.7-10.8-10.3	6.84-13.98-12.2
8	Aug. 07, 2009 Test 2	6-21-37	5.6-5/7-5.4	7.95-12.64-28.23

The processed pouches were stored at 4°C. Pouches left after microbiological testing for various pathogens were shipped on ice to Natick on 10-14-2009.

4.3. Conventional retort processing

A trial batch of the product was made during week of July 27-31 for a preliminary processing run at Seattle SPA facility. The full production batch of plastic and aluminum laminate pouches was sent to Seattle via refrigerated truck on August 4. The summary of the conventional retort processing provided by Subba Rao Gurram and Kenny Lum (SPA, Seattle, WA) is included in the Appendix 2.

The appearance of the pouches after microwave and retort sterilization is shown in Fig 4.2.

Fig. 4.2. Appearance of the pouches after processing: left to right: plastic laminate after microwave processing, aluminum laminate after conventional retort processing, plastic laminate after conventional retort processing.

5. Microbiological testing for chicken dumplings product processed in microwave sterilization system at WSU

5.1. Microbiological testing requirements

According to instructions provided by Dr. C. Patrick Dunne, the following testing had to be performed for the processed in microwave sterilization system pouches: testing of spores, Salmonella, Listeria and incubation of product at 35°C for 10 days. (Fig. 5.1).

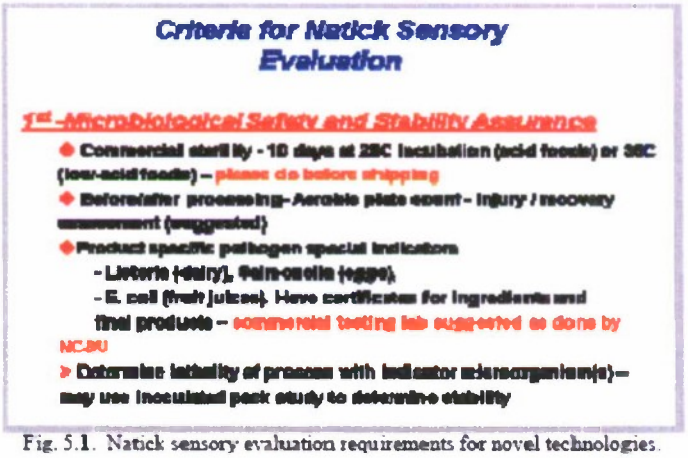


Fig. 5.1. Natick sensory evaluation requirements for novel technologies.

All microbiological testing for spores, Salmonella, and Listeria were performed by the third party: Silliker Inc. (Cypress, CA). Incubation of pouches was done at WSU (Fig. 5.2)

Fig. 5.2. Incubation of the processed pouches at 35°C for 10 days

5.2. Mesophillic and Thermophillic aerobic and anaerobic spore testing

A total of 16 pouches (2 from each one of 8 runs) were sent to Silliker Inc (Cypress, CA) for total spore count and thermophile spore survival evaluation. This sample size was suggested by Silliker microbiologist Lynne Kuchel to sufficiently represent the entire microwave processing batch. Results of microbiological evaluation were negative for mesophillic and thermofillic aerobic and anaerobic spores. Full report from Silliker Inc is provided in Appendix 3.

5.3. Salmonella and Listeria testing

A total of 8 pouches (1 randomly selected pouch from each run) were sent to Silliker Inc (Cypress, CA) for Salmonella and Listeria testing. All samples analyzed were negative for Salmonella and Listeria. Full report from Silliker Inc for Listeria and Salmonella testing is provided in Appendix 4.

5.4. Incubation studies at 35°C

A total of 8 pouches (1 randomly selected pouch from each run) were placed at 35 °C for observation on 08-21-09. The number of pouches was selected according to USDA commercial requirements, 9 CFR 318.309(d)(1)(iv) Incubation samples.

> (a) From each load of product processed in a batch-type thermal processing system (still or agitation), the establishment shall select at least one container for incubation.
>
> (b) For continuous rotary retorts, hydrostatic retorts, or other continuous-type thermal processing systems, the establishment shall select at least one container per 1,000 for incubation 9 CFR 318.309(d)(1).

In order to satisfy statistical sampling guidelines for "ANSI/ASQC Z1.4 Performance Without Limit Numbers" used by Natick, sample size was increased. Five additional, randomly selected pouches were added to the incubation at 35 °C on 08-28-09 (as per CW4 Greg M. Burnham's recommendations).

> "12 or 13 which would provide about a 95% assurance the product was pathogen free...the described 8 samples would only give a 90% assurance level (ref http://guidebook.dcma.mil/226/tools_links_file/stat-sample.htm). These numbers are based on the old Mil Std 105E - Statistical Sampling which is now sold by the American Society for Quality as "ANSI/ASQC Z1.4 Performance Without Limit Numbers" (e-mail form Dr. Burnham). Reference for statistical sampling is provided in Appendix 5.

Incubation of total of 13 pouches at 35°C for 10 days did not reveal any signs of package bulging. Observations were repeated at 3 weeks and 4 weeks of incubation: no pouches exhibited bulging with longer incubation time.

6. Labeling of pouches

The inkjet printer JET2SE (Leibinger, Germany) provided by Printpack Inc (Fig. 6.1) was used to label the pouches processed in the microwave sterilization system at WSU. Pouches were labeled with the following information: year/month/date of processing/ run#/ pouch #/place of production/process type/product name.

Fig. 6.1. Labeling of pouches at WSU.

Pouches processed in conventional retort were labeled with a stick-on labels provided by WSU. Labels indicated type of processing, type of laminate and pouch #.

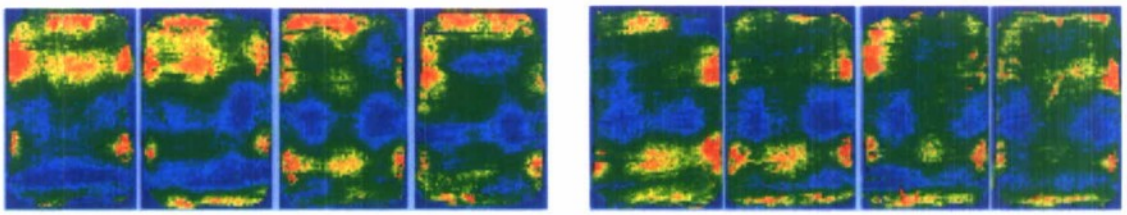
Appendixes

Appendix 1.

3.2.1. Comparison of heating patterns in alternative size pouches (filled with solid whey protein gel) in holders with and w/o snaps (report draft)

The influence of the metal snap fasteners on heating pattern was investigated by comparing heating patterns and cold spot locations in whey protein gel (WPG) Alternate pouches processed in holders with and w/o snap fasteners. 8-oz WPG sample was filled in each Alternate pouch (Fig. 3.2). The pouches were placed in sample holders with and w/o snap fasteners and processed in the MW system under the selected conditions (power set: 7.5/7.5/4.7/4.7 kW, moving speed: 31 inch/min, water temperature: 72/124/123$_o$C). The processed trays were used for heating pattern analysis using computer vision methods. Heating patterns in the WPG pouches processed both with and w/o snap fasteners were similar (Fig 3.3), and cold spot locations for the two cases were almost same: (23.4, -6.1) mm and (23.9, -6.4) mm, respectively (Tables 3.1 & 3.2).

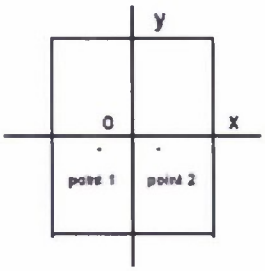
Fig. 3.2 WPG sample and alternative size 8oz pouch



(a) with snap fasteners (June 16 test 1) (b) w/o snap fasteners (June 18 test 1)

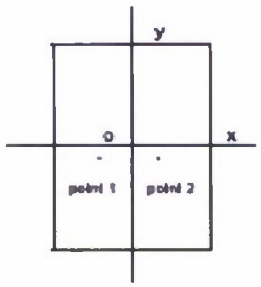
Fig. 3.3 Sample heating patterns of WPG pouches processed with and w/o metal snap fasteners

Table 3.1 Summary of cold spot locations in Alternate WPG pouches (with snaps)



Run #	Pouch #	Point 1			Point 2		
		Color value	x_1	y_1	Color value	x_2	y_2
June 16 2009 test 1	5	58.0	-24.7	-4.2	55.7	25.2	-1.3
	6	57.9	-22.2	-4.3	19.0	24.5	-1.5
	7	19.7	-22.6	-5.8	18.7	27.1	-5.3
	8	40.6	-22.8	-14.7	23.1	22.0	-9.6
June 16 2009 test 2	5	45.3	-18.5	-14.0	30.4	25.6	-8.1
	6	40.8	-15.4	-15.3	17.1	18.1	-9.2
	7	65.5	-18.5	-4.6	8.8	17.2	-4.5
	8	67.1	-21.3	-2.2	34.3	25.0	-5.2
June 18 2009 test 1	11	20.8	-24.0	-11.7	25.0	25.3	-5.6
	12	40.7	-24.8	-10.6	46.9	23.3	-6.7
	13	52.6	-24.2	-15.2	14.4	23.0	-8.2
Ave		46.4	-21.7	-9.3	26.7	23.4	-6.1
Stdev		16.0	3.0	5.2	14.2	3.2	2.9

Table 3.2 Summary of cold spot locations in Alternate WPG pouches (w/o snaps)



Run #	Pouch #	Point 1			Point 2		
		Color value	x_1	y_1	Color value	x_2	y_2
June 18 2009 test 1	3	27.9	-21.7	-9.6	30.9	19.2	-7.6
	4	19.6	-23.8	-7.8	15.2	24.1	-6.6
	5	32.0	-20.1	-7.1	34.6	26.6	-4.9
	6	30.6	-25.8	-7.0	21.1	23.6	-7.7
	7	15.7	-21.3	-5.6	18.7	25.0	-3.1
	8	57.4	-19.4	-8.6	63.2	26.5	-5.5
	9	51.3	-31.8	-7.1	35.7	24.6	-6.7
	10	44.9	-16.2	-15.9	17.2	21.5	-9.0
Ave		34.9	-22.5	-8.6	29.6	23.9	-6.4
Stdev		14.9	4.7	3.2	15.8	2.5	1.8

3.2.2. Determination of cold spot in alternative size pouches by using WPG pieces and sauce

To simulate the processing of pouches of chicken & dumplings with sauce, pouches filled with WPG pieces and sauce were processed and detected for the heating patterns. In the pouch (128 g WPG pieces + 99 g sauce), two of the four WPG pieces were placed at the cold areas identified by the tests with solid-WPG pouches (Fig. 3.4 b). Fig. 3.4 c shows a sample heating pattern inside pouches filled with WPG pieces and sauce. The cold spot location in the pouches of WPG pieces and sauce was detected at (23.3, -3.9) mm (Table 3.3), which was close to the cold spot location, (23.4, -6.1) mm, identified by the solid WPG (Table 3.1).

3.3. Development and test of Ultem frame holders for supporting Ellab sensors in Alternative size pouches (Task A.4 in proposal)

Based on the identified cold spot location, (23.4, -6.1) mm from the central point inside the Alternate pouch, four Ultem frame holders for supporting Ellab sensors in Alternate pouches were made (Fig. 3.5). The holder holds the Ellab sensor inside the pouch and fixes the Ellab sensor tip at the cold spot location.
Tests were done on WPG pouches with and w/o Ultem frame holders & Ellab sensors. There was no difference between the heating patterns inside the WPG pouches both with and w/o the holder & Ellab. This suggested that use of the Ultem frame holder and Ellab sensor did not affect the MW processing.

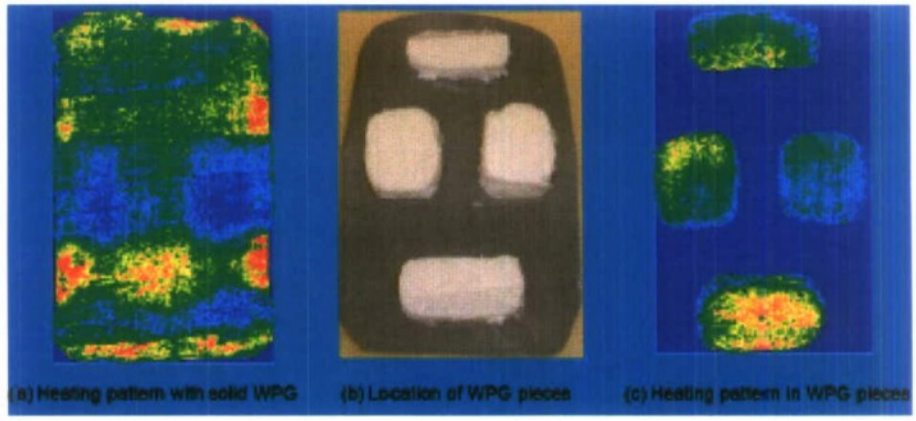
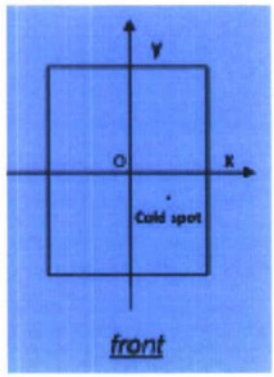


Fig 3.4 Location of WPG pieces and sample heating patterns measured from solid-WPG pouches and pouches filled with WPG-pieces & sauce

Table 3.3 Summary of cold spot location measured by WPG pieces and sauce



July 24 - test1	Color value	X	Y
Pouch 1	66.7	24.2	2
Pouch 2	45.5	22.8	8
Pouch 3	45.6	25.3	-4.4
Pouch 4	62.8	21.1	-4.9
Pouch 5	77.2	23.1	0
Ave	59.6	23.3	-3.9
Stdev	13.8	1.6	3.0

Fig. 3.4 Ultem frame holder with Ellab sensor and Alternate pouch

3.4. Development of schedules for processing chicken & dumpling pouches (Task A.5 in proposal)

With chicken and dumpling pouches, heat penetration (HP) tests were conducted to determine the process schedule to deliver the target F_0 of 6.0 min. An Ellab sensor was used to record the temperature profile at the cold spot inside a selected pouch (Fig. 3.5).

Tests were performed under the following selected conditions (schedule):

- 8-oz Printpack® Alternate pouch
- Weight of chicken, dumplings and sauce: 227 g (8 oz)
- MW power set: 7.5 / 7.5 / 4.7 / 4.7 kW for 4 MW heating cavities
- Moving speed: 35 inch/min
- Water temperature: 72/124/123 °C for preheating/MW heating/holding sections
- System pressure: 34 psig
- Pre-heating time: 30 min
- Cooling time: 5 min

Fig. 3.5 Ellab sensor placed in chicken & dumpling pouch

Fig. 3.6 provides a sample temperature profile recorded by the Ellab sensor. The average F_0 at the cold spot from three test runs was 6.8 min. The result confirmed that the processing schedule used for the HP tests could provide the MW processing on the 8-oz chicken & dumpling pouches to achieve the target F_0 of 6 min.

Appendix 2.

SCS Inc
FOOD CONSULTING SERVICES

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August 21, 2009

Dr. Juming Tang
Professor, Scientist

Biological Systems Engineering Department
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Pullman, Washington 99164-6120
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Ref: Short summary of the "chicken & dumplings packed in pouches" project

Dear Dr. Tang

This is a brief summary of the "chicken & dumplings packed in pouches" project that we worked in July and August 2009.

We have conducted the feasibility studies for processing chicken & dumplings packed in retort pouches using saturated steam and/or steam/air retort systems. We have also conducted the heat penetration studies to develop the schedule processes. Also we processed a commercial batch of 500 pouches at one of our member facilities.

Two types of pouches: Plastic and Aluminum were tested to evaluate the feasibility and the effectiveness of the process inside the retort.

Two types of processing mediums: Saturated steam and steam/air over pressure

Test conditions and results:

Test Run1: conducted at 241^{0}F

Initial Temperature (IT) = 35^{0}F Product thickness = 1 inch
Residual Air = 6 cc **Sterilizing value, F_s = 6**

Processing medium	Process Temp (°F)	Time (min)
Saturated Steam	240	54
	245	43
	250	36

Heating Factors: J = 1.74 and F_h = 17.3

Test Run2: conducted at 240^{0}F

Initial Temperature = 35^{0}F Product thickness = 1 inch

Residual Air = 15 cc **Sterilizing value, F_o = 6**

Processing medium	Process Temp (^{0}F)	Time (min)
Saturated Steam	240	55
	245	44
	250	37

Heating Factors: J = 1.61 and F_i = 18.2

Figure 3 Pouches with higher residual air processed in saturated steam

Test Run3: conducted at 239^{0}F with steam/air over pressure of 3.5 psig*

Initial Temperature = 35^{0}F Product thickness = 1 inch

Residual Air = 12 to 15 cc Retort pressure = 13.2 to 13.5 psig

Sterilizing value, F_0 = 6

Processing medium	Process Temp (^{0}F)	Time (min)
Steam/Air Overpressure	240	59
	245	47
	250	40

*Gauge pressure of saturated steam at 240^{0}F = 10 psig

Heating Factors: J = 1.40 and F_h = 21.2

Figure 4: Pouches processed with steam/air overpressure

Processes conducted at commercial processing facility:

Swinomish Fish Co.,
La Conner, WA.

Test Run1: conducted at 240^{0}F with an over pressure of 3 to 3.5 psig

No of Pouches = 30 (15 plastic and 15 aluminum)

Initial Temperature = 35^{0}F Product thickness = 1 inch

Residual Air = 10 to 12 cc Retort pressure = 13.5 psig

Process time = 62 min

Run2: conducted at 240^{0}F with an ove· pressure of 2 to 2.5 psig

No of Pouches = 500 (250 plastic and 250 aluminum)

Initial Temperature = 35^{0}F Product thickness = 1 inch

Residual Air = 10 to 12 cc Retort pressure = 12.5 psig

Process time = 67 min

Appendix 3.

SILLIKER
Food Safety & Quality Solutions
SILLIKER, Inc.
Southern California Laboratory
6360 Gateway Drive, Cypress, CA 90630
Tel. 714 226 0001 Fax. 714 226 0009

CERTIFICATE OF ANALYSIS

COA No:	SCA-3314785-0
Supersedes:	None
COA Date	8/15/09
Page 1 of 5	

COPY TO:
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ORIGINAL TO:
Mr. Kyle Tatum
Senior Quality Engineer
Printpack Inc
3551 Lee Hill Drive
Fredericksburg, VA 22408

Received From:	Villa Rica, GA
Received Date:	8/12/09

Location of Test: (except where noted)
Cypress, CA

Analytical Results

Desc. 1: Sample #1 — **Laboratory ID:** 3177928 82
Desc. 2: Aug 5-2009 — **Condition Rec'd:** NORMAL
Desc. 3: Run 2 — **Temp Rec'd (°C:** 6.9
Desc. 4: Pouch 1 Of 39
Desc. 5: Chicken Dumplings

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN 3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/6)	0/6 Tubes Positive	-	CMMEF, 4th ed.	8/15/09	

Desc. 1: Sample #2 — **Laboratory ID:** 3177928 90
Desc. 2: Aug 5-2009 — **Condition Rec'd:** NORMAL
Desc. 3: Run 2 — **Temp Rec'd (°C:** 6.9
Desc. 4: Pouch 2 Of 39
Desc. 5: Chicken Dumplings

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN 3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/6)	0/6 Tubes Positive	-	CMMEF, 4th ed.	8/15/09	

Desc. 1: Sample #3 — **Laboratory ID:** 3177928 98
Desc. 2: Aug 5-2009 — **Condition Rec'd:** NORMAL
Desc. 3: Run 2 — **Temp Rec'd (°C:** 6.9
Desc. 4: Pouch 1 Of 32
Desc. 5: Chicken Dumplings

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN 3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/6)	0/6 Tubes Positive	-	CMMEF, 4th ed.	8/15/09	

SILLIKER
Food Safety & Quality Solutions

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CERTIFICATE OF ANALYSIS

COA No:	SCA-33167485-0
Supersedes:	None
COA Date	8/15/09
Page 2 of 6	

COPY TO:
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ORIGINAL TO:
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Senior Quality Engineer
Printpack Inc.
3551 Lee Hill Drive
Fredericksburg, VA 22408

Received From:	Villa Rica, GA
Received Date:	8/12/09

Location of Test: (except where noted)
Cypress, CA

Analytical Results

Desc. 1: Sample #4 — Laboratory ID: 317792150
Desc. 2: Aug 6-2009 — Condition Rec'd: NORMAL
Desc. 3: Run 3 — Temp Rec'd (°C): 6.9
Desc. 4: Pouch 2 Of 22
Desc. 5: Chicken Dumplings

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN 3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/6)	0/6 Tubes Positive	-	CMMEF, 4th ed.	8/16/09	

Desc. 1: Sample #5 — Laboratory ID: 317792203
Desc. 2: Aug 6-2009 — Condition Rec'd: NORMAL
Desc. 3: Run 1 — Temp Rec'd (°C): 6.9
Desc. 4: Pouch 1 Of 22
Desc. 5: Chicken Dumplings

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN 3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/6)	0/6 Tubes Positive	-	CMMEF, 4th ed.	8/16/09	

Desc. 1: Sample #6 — Laboratory ID: 317792206
Desc. 2: Aug 6-2009 — Condition Rec'd: NORMAL
Desc. 3: Run 1 — Temp Rec'd (°C): 6.9
Desc. 4: Pouch 2 Of 22
Desc. 5: Chicken Dumplings

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN 3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/6)	0/6 Tubes Positive	-	CMMEF, 4th ed.	8/16/09	

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CERTIFICATE OF ANALYSIS

COA No:	SCA-3316786-0
Supersedes:	None
COA Date	8/15/09
Page 3 of 6	

COPY TO:
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Fredericksburg, VA 22408

Received From:	Villa Rica, GA
Received Date:	8/12/09

Location of Test: (except where noted) Cypress, CA

Analytical Results

Desc. 1: Sample #7 — Laboratory ID: 317792212
Desc. 2: Aug 6-2009 — Condition Rec'd: NORMAL
Desc. 3: Run 2 — Temp Rec'd [°C]: 6.9
Desc. 4: Pouch 1 Of 31
Desc. 5: Chicken Dumplings

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/6)	0/6 Tubes Positive	-	CMMEF, 4th ed.	8/15/09	

Desc. 1: Sample #8 — Laboratory ID: 317792216
Desc. 2: Aug 6-2009 — Condition Rec'd: NORMAL
Desc. 3: Run 2 — Temp Rec'd [°C]: 6.9
Desc. 4: Pouch 2 Of 31
Desc. 5: Chicken Dumplings

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/6)	0/6 Tubes Positive	-	CMMEF, 4th ed.	8/15/09	

Desc. 1: Sample #9 — Laboratory ID: 317792224
Desc. 2: Aug 6-2009 — Condition Rec'd: NORMAL
Desc. 3: Run 3 — Temp Rec'd [°C]: 6.9
Desc. 4: Pouch 1 Of 31
Desc. 5: Chicken Dumplings

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/6)	0/6 Tubes Positive		CMMEF, 4th ed.	8/15/09	

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CERTIFICATE OF ANALYSIS

COA No:	SCA-33167885-0
Supersedes:	None
COA Date:	8/19/09
Page 4 of 6	

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Received Date:	8/12/09

Location of Test: (except where noted)
Cypress, CA

Analytical Results

Desc. 1: Sample #10
Desc. 2: Aug 6-2009
Desc. 3: Run 3
Desc. 4: Pouch 2 Of 31
Desc. 5: Chicken Dumplings
Laboratory ID: 317792228
Condition Rec'd: NORMAL
Temp Rec'd (°C): 6.9

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN 3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/5)	0/5 Tubes Positive	-	CMMEF, 4th ed.	8/15/09	

Desc. 1: Sample #11
Desc. 2: Aug 6-2009
Desc. 3: Run 4
Desc. 4: Pouch 1 Of 31
Desc. 5: Chicken Dumplings
Laboratory ID: 317792226
Condition Rec'd: NORMAL
Temp Rec'd (°C): 6.9

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN 3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/5)	0/5 Tubes Positive	-	CMMEF, 4th ed.	8/15/09	

Desc. 1: Sample #12
Desc. 2: Aug 6-2009
Desc. 3: Run 4
Desc. 4: Pouch 2 Of 31
Desc. 5: Chicken Dumplings
Laboratory ID: 317792243
Condition Rec'd: NORMAL
Temp Rec'd (°C): 6.9

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN 3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/5)	0/5 Tubes Positive	-	CMMEF, 4th ed.	8/15/09	

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Page 6 of 6	

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Received Date:	8/12/09

Location of Test: (except where noted)
Cypress, CA

Analytical Results

Desc. 1:	Sample #16	Laboratory ID:	317782279
Desc. 2:	Aug 7-2009	Condition Rec'd:	NORMAL
Desc. 3:	Run 2	Temp Rec'd (°C):	6.9
Desc. 4:	Pouch 2 Of 23		
Desc. 5:	Cheddar Dumplings		

Analyte	Result	Units	Method Reference	Test Date	Loc.
Mesophilic Aerobic Spores	<1.0	/g	CMMEF, 4th ed.	8/14/09	
Mesophilic Anaerobic Spores - MPN 3	<3	/g	CMMEF, 4th ed.	8/14/09	
Thermophilic Aerobic Spores	<5	/10g	CMMEF, 4th ed.	8/14/09	
Thermophilic Anaer. Spores (Pos/6)	0/6 Tubes Positive	-	CMMEF, 4th ed.	8/15/09	

Jorge Hernandez — Chemistry Operations Manager

Appendix 4.

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COA No	SCA-33200701-0
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COA Date	8/31/09
Page 1 of 2	

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Received Date:	8/28/09

Location of Test: (except where noted)
Cypress, CA

Analytical Results

Desc. 1:	Sample Code: 0805-2-3			Laboratory ID:	318419944
Desc. 2:	Chicken Dumplings			Condition Rec'd:	NORMAL
Desc. 3:	Aug 05 Run 2			Temp Rec'd (°C):	5.0
Analyte		**Result**	**Units**	**Method Reference**	**Test Date** **Loc.**
Genus Listeria - ELFA		Negative	/25g	AOAC 999.06	8/31/09
Salmonella - ELFA		Negative	/25g	AOAC 2004.03	8/31/09
Desc. 1:	Sample Code: 0805-3-3			Laboratory ID:	318419945
Desc. 2:	Chicken Dumplings			Condition Rec'd:	NORMAL
Desc. 3:	Aug 05 Run 3			Temp Rec'd (°C):	5.0
Analyte		**Result**	**Units**	**Method Reference**	**Test Date** **Loc.**
Genus Listeria - ELFA		Negative	/25g	AOAC 999.06	8/31/09
Salmonella - ELFA		Negative	/25g	AOAC 2004.03	8/31/09
Desc. 1:	Sample Code: 0805-1-3			Laboratory ID:	318419963
Desc. 2:	Chicken Dumplings			Condition Rec'd:	NORMAL
Desc. 3:	Aug 05 Run 1			Temp Rec'd (°C):	5.0
Analyte		**Result**	**Units**	**Method Reference**	**Test Date** **Loc.**
Genus Listeria - ELFA		Negative	/25g	AOAC 999.06	8/31/09
Salmonella - ELFA		Negative	/25g	AOAC 2004.03	8/31/09
Desc. 1:	Sample Code: 0805-2-3			Laboratory ID:	318419963
Desc. 2:	Chicken Dumplings			Condition Rec'd:	NORMAL
Desc. 3:	Aug 05 Run 2			Temp Rec'd (°C):	5.0
Analyte		**Result**	**Units**	**Method Reference**	**Test Date** **Loc.**
Genus Listeria - ELFA		Negative	/25g	AOAC 999.06	8/31/09
Salmonella - ELFA		Negative	/25g	AOAC 2004.03	8/31/09
Desc. 1:	Sample Code: 0805-3-3			Laboratory ID:	318419967
Desc. 2:	Chicken Dumplings			Condition Rec'd:	NORMAL
Desc. 3:	Aug 05 Run 3			Temp Rec'd (°C):	5.0
Analyte		**Result**	**Units**	**Method Reference**	**Test Date** **Loc.**
Genus Listeria - ELFA		Negative	/25g	AOAC 999.06	8/31/09
Salmonella - ELFA		Negative	/25g	AOAC 2004.03	8/31/09

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Supersedes:	None
COA Date	8/31/09
Page 2 of 2	

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Received From:	Orange, TX
Received Date:	8/25/09

Location of Test: (except where noted)
Cypress, CA

Analytical Results

Desc. 1:	Sample Code: 0808-4-3			Laboratory ID:	318019971	
Desc. 2:	Chicken Dumplings			Condition Rec'd:	NORMAL	
Desc. 3:	Aug 08 Run 4			Temp Rec'd (°C):	5.0	
Analyte		**Result**	**Units**	**Method Reference**	**Test Date**	**Loc.**
Genus Listeria - ELFA		Negative	/25g	AOAC 999.06	8/31/09	
Salmonella - ELFA		Negative	/25g	AOAC 2004.03	8/31/09	
Desc. 1:	Sample Code: 0807-1-3			Laboratory ID:	318019976	
Desc. 2:	Chicken Dumplings			Condition Rec'd:	NORMAL	
Desc. 3:	Aug 07 Run 1			Temp Rec'd (°C):	5.0	
Analyte		**Result**	**Units**	**Method Reference**	**Test Date**	**Loc.**
Genus Listeria - ELFA		Negative	/25g	AOAC 999.06	8/31/09	
Salmonella - ELFA		Negative	/25g	AOAC 2004.03	8/31/09	
Desc. 1:	Sample Code: 0807-2-3			Laboratory ID:	318019979	
Desc. 2:	Chicken Dumplings			Condition Rec'd:	NORMAL	
Desc. 3:	Aug 07 Run 2			Temp Rec'd (°C):	5.0	
Analyte		**Result**	**Units**	**Method Reference**	**Test Date**	**Loc.**
Genus Listeria - ELFA		Negative	/25g	AOAC 999.06	8/31/09	
Salmonella - ELFA		Negative	/25g	AOAC 2004.03	8/31/09	

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Appendix 5.

STATISTICAL SAMPLING

Source (http://guidebook.dcma.mil/226/tools_links_file/stat-sample.htm) Since the cancellation MIL-STD-105E, the availability of statistically sound, sampling tables to personnel performing in-process and end item product audits has been scarce. Most people performing these audits today, are still using tables from this canceled document or are using Contractor's Sampling Tables. The table below is approved for use by DCMA QA personnel performing zero-based sampling. If no AQL is contractually specified, an AQL of 1.0% is suggested.

ZERO-BASED ACCEPTANCE SAMPLING PLAN

"A Indicates that the Entire Lot Must be Inspected

Acceptable Quality Level (AQL)

LOT SIZE	.010%	.015%	.025%	.040%	.065%	.10%	.15%	.25%	.40%	.65%	1.0%	1.5%	2.5%	4.0%	6.5%	10.0%
1-8	A	A	A	A	A	A	A	A	A	A	A	A	5	3	2	2
9-15	A	A	A	A	A	A	A	A	A	A	13	8	5	3	2	2
16-25	A	A	A	A	A	A	A	A	A	20	13	8	5	3	3	2
26-50	A	A	A	A	A	A	A	A	32	20	13	8	5	5	5	2
51-90	A	A	A	A	A	A	80	50	32	20	13	8	7	6	5	4
91-150	A	A	A	A	A	125	80	50	32	20	13	12	11	7	6	5
151-280	A	A	A	A	200	125	80	50	32	20	20	19	13	10	7	6
281-500	A	A	A	315	200	125	80	50	48	47	29	21	16	11	9	7
501-1200	A	800	500	315	200	125	80	75	73	47	34	27	19	15	11	8
1201-3200	1250	800	500	315	200	125	120	116	73	53	42	35	23	18	13	9
3201-10,000	1250	800	500	315	200	192	189	116	86	68	50	38	29	22	15	9
10,001-35,000	1250	800	500	315	300	294	189	135	108	77	60	46	35	29	15	9
35,001-150,000	1250	800	500	400	476	294	218	170	123	96	74	56	40	29	15	9
150,001-500,000	1250	800	750	715	476	345	270	200	156	119	90	64	40	29	15	9
500,001 & Over	1250	1200	1112	715	556	435	303	244	189	143	102	64	40	29	15	9

Other Available Sources - There are some documents that are currently available that can be used that contain certified statistically sound sampling tables.

1. ZERO ACCEPTANCE NUMBER SAMPLING PLANS fourth edition by Nicholas L. Squeglia. This book gives a number of zero based sampling plans and their corresponding Operating Characteristic (OC) Curves and Values. It is the

state of the art in zero based sampling plans. It's only draw back is (as with all zero based sampling plans) the OC curves flatten out at the bottom. This means when the probability of you accepting a bad lot goes down to approximately 10% or below, you would be more apt to accept a bad lot using a zero based sampling plan. This document is made available by ASQC, Quality Press, 611 East Wisconsin Avenue, Milwaukee, Wisconsin 53202

2. MIL-STD-1916, DoD PREFERRED SAMPLING PLANS FOR ACCEPTANCE OF PRODUCT This document contains a set of statistically sound sampling plans and procedures for planning and conducting the inspection of product to assess quality and provide information of conformance to contract requirements. This new military standard complies with the Department of Defense policy of eliminating acceptable quality levels (AQLs) and associated practices. The standard is currently available, however, the handbook addressing this standard and providing clarification is still being written. Also, some of these plans may be too stringent to use, based on contract requirements.

3. Electronic Industries Association (EIA) Standard, ZERO ACCEPTANCE NUMBER SAMPLING PROCEDURES AND TABLES FOR INSPECTION BY ATTRIBUTES BY A CONTINUOUS MANUFACTURING PROCESS Since conventional attribute sampling plans based on nonzero acceptance are no longer desirable, this industry standard places an emphasis on zero based sampling plans as they relate to Lot Tolerance Percent Defective (LTPD) value or the limiting quality protection of MIL-STD-105. The OC curves of this document are for the most part equal to or better than their associated MIL-STD-105 curves. Published by Electronic Industries Association, Engineering Department, 2001 Pennsylvania Ave. N.W., Washington, D.C. 20006. EIA Standard Sales Dept (202/457-4966).

You may wish to note if you still have contracts which require MIL-STD-105, American Society for Quality Control, now has available, ASQC Z1.4. a virtual exact copy of MILSTD- 05E.

Remember also, that in order to use the Contractor's sampling plan, the plan shall afford us equal or better protection that the requirements of the contract.

Annex 6. Nanocomposite Polyolefins for Improved WVTR

Abstract:

Schirmer et al. (2008) reported water vapor transmission rate (WVTR) improvements in cast polypropylene (PP) film by careful compounding of Montmorillonite platelets into PP resin. This work was reproduced and additional improvements sought by using PP-polynorborene (a cyclic olefin copolymer or "COC") blends. The composite clay-PP-COC materials were too brittle for extrusion as a monolayer film, but could be coextruded between two skin layers of PP.

Keywords:

nanocomposite, polynorborene, polypropylene, cyclic olefin copolymers, WVTR

Background:

Various clay platelets intercalated and compounded into polymers with polar groups (such as ethylene vinyl alcohol-"EVOH" and nylon) that are capable of associative interactions (e.g. Lewis acid Lewis-base interactions, hydrogen bonding) lead to barrier enhancement of he polymer, particularly oxygen barrier. (Thellen et al. 2006, Cabado, 2004). Similar attempts with various nanoplatelets in the non-polar polyolefins have not fared as well, and present significantly greater hurdles to accomplish (Ton-That et al., 2004). Polypropylene (PP)-clay hybrids were prepared by Kawasumi et al. (1997) by simple melt-mixing of three components, i.e., PP, maleic anhydride modified polypropylene oligomers (PP-MA), and clays intercalated with stearylammonium. They found that there are two important factors to achieve the exfoliated and homogeneous dispersion of the layers in the hybrids: (1) the intercalation capability of the oligomers in the layers and (2) the miscibility of the oligomers with PP. Almost complete hybrids were obtained in the case where the PP-MA has both intercalation capability and miscibility.

In effect, the polyolefin challenges are addressed with compatiblizers, additives that "tie" the polar platelets to the nonpolar polymer chains. The nonpolar ends of the maleic anhydride modified polypropylene (MAMP) oligomers blend into the PP matrix and their polar ends interact with the polarity of the clay platelets. Additionally, the platelets assume an essentially planar orientation in the polymer matrix. Compounding and extrusion conditions (temperature, shear, pressure, etc.) greatly influence this effect.

Schirmer et al. (2008) compounded PP with 7.5% montmorillonite layered silicate (MLS) and 2.5% MAMP and extruded this blend to produce cast nanocomposite films. Specific materials used are listed in Table 1.The addition of the MLS nanoparticles under experimental conditions improved the thermal, mechanical and barrier properties of film.

TABLE 1
PP/MLS/MAMP Blend by reported by Schirmer *et. al* (2008)

	PP	MAMP	MLS
Supplier	Huntsman	Eastman	So. Clay Prods. Inc.
Grade	P4G2Z-159	Epolene G-3003	Cloisite® 20A
Nominal percentage	90.1	1.6	7.5

Polynorborene (COC) (Fig. A) provides better barrier to water vapor (lower WVTR) than linear polypropylenes (Lamont, 2000). Tatarka (2008) reported that COC-linear low density polyethylene (LLDPE) polyolefins blends had WVTR values intermediate between the values provided by neat COC and the LLDPE itself. Wu and Wu (2005) were able to prepare COC-clay nanocomposites using solution mixing (rather than melt processing). They reported significantly improved water-barrier (MVTR 54-62% less) property compared to neat COC.

Preliminary work for non-foil barrier packaging research indicated that while plastic barrier structures could approach the US Army target oxygen barrier values (Ratto, 2006) (OTR $\leq$0.06 cc•day/m^2), the water vapor barrier level (OTR $\leq$0.01 gm•day/m^2) could not be attained with available materials. Lower WVTR sealant layers were sought by first trying to replicate the results of Schirmer *et. al.* (2008) and then evaluating possible synergies of nanocomposites with polypropylene/polynorborene blends.

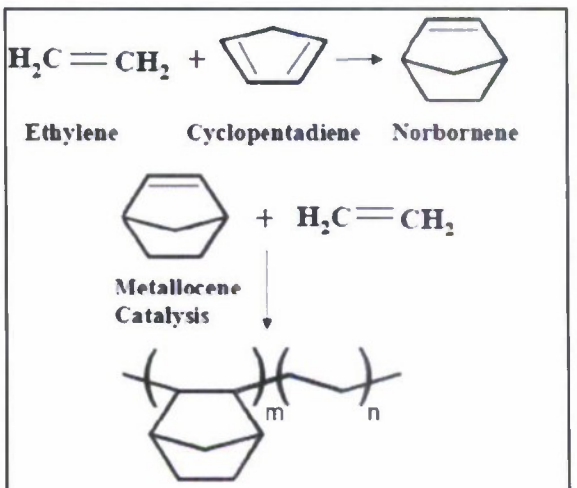


Figure A
Synthesis and Structure of the cyclic olefin copolymer, Polynorborene (after Lamont, 2000)

Methods and Materials

Two compounders produced nanocomposites of modified clay nano-platelets with PP and with PP/COC blends. Preliminary assessments by the compounders were used to select two blends by each to evaluate as cast films.

Blend Processing

Rhetech (Whitmore Lake, MI) was chosen based on prior work (Karian, 2008) to produce modified Montmorillonite nanoclay compounded into PP and PP –COC blends. Two levels of the nanoclay were used at 6 % and 8 % of total weight. In addition to the two levels of nanoclay, two different COC products were tested; Topas 5013X14 (230°C Melt Index [MI] = 11) and 6013F-04 (MI=2.3). Six blends were produced by Rhetech (Table2). The detailed report from Rhetech on the blend processability is available on request..

TABLE 2
PP/MLS and PP-COC/MLS Blends by Rhetech:
Nominal Composition (wt.%)

Supplier	PP Basell	COC Topas	COC Topas	Compatiblizer Eastman	Clay S. Clay Prods.
Grade→ Sample↓	*SA-861*	*5013X14*	*6013F-04*	*Epolene G-3003*	*Cloisite® 20A*
5462#	89			5	6
5467J	87			5	8
5468J	26.7	62.3		5	6
5470J	26.1	60.9		5	8
5473J	26.7		62.3	5	6
5476J	26.1		60.9	5	8

Nanobiomatters (NBM, Valencia, Spain) was also chosen to evaluate their proprietary treatednanoclays compounded into PP and PP–COC blends. They initially considered three different nanoclays; Nanobioter® 202 A1.41; Nanobioter® 202 A1.49, and Nanobioter® 404 C1.33, and then added a fourth for consideration, Nanobioter® 434 C1.33. Both of the 202-grade clays are food contact compliant organic-modified montmorillonite clays (oMMT's.) The 400-series grades are also food contact compliant and specifically developed for polyolefins so as to require no compatibilizers. The 404-grade shows extremely enhanced thermal stability in the products and has been

designed for packaging applications in the food contact layer since it is believed not to affect the organoleptic properties of the packaged contents. Further characterization of the NBM products is pending patent action on European patent application 1,985,585 A1 (Lagaron et al. 2008).

The 202 grade samples were produced in two steps. First a masterbatch of nanoclay was prepared introducing the compatibilizer and a fraction of the polymer. As a second step the masterbatch was diluted with the rest of the polymer to a final inorganic clay concentration of 8%. The samples containing 404/434 grades were directly prepared with a final inorganic clay concentration of 8%. Table 3 summarizes the ten blends produced by NBM. A detailed report from NBM on the blend processability is available on request.

TABLE 3
PP/MLS and PP-COC/MLS Blends by NBM:
Nominal Composition (wt.%)

Supplier	PP Basell	COC Topas	Compatiblizer Eastman	Clay NBM	Clay NBM	Clay NBM	Clay NBM
Grade→ Sample↓	*SA-861*	*6013F-04*	*Epolene G-3003*	202 A1.41	202 A1.49	404 C1.33	434 C1.33
E09022401*	92	0	0			8	
E09022406	29.3	62.7	0			8	
E09040102	89.5	0	2.5	8			
E09040103	26.8	62.7	2.5	8			
E09040101	89.5		2.5		8		
E09030603	26.8	62.7	2.5		8		
E09051302	93.5	0	2.5	4			
E09051202	92	0	0				8
E09051201	27.5	64.5	0				8
E09052601*	26.8	62.7	2.5				8

* Blends forwarded for film extrusion

Film extrusion:

Printpack extruded films using the Rhetech and NBM blends on Printpack's pilot plant's 12 in (305 mm) flat die (EDI "Fast Gap") cast film line. The line comprises 4 single screw extruders, 2 at 1.25 inch (31.8 mm), and 2 at 1 inch (25.4 mm). A feed block combining adapter can be configured to provide up to seven layer film. All films were extruded to a nominal 100μ (4 mil) thickness. The extrusion profile was set from 400°F (204°C) to 480°F (249°C) from the feed throat through the adapter, and at 460°F (238°C) through the adapter and die.. All four of the Rhetech PP-COC/MLS blends were too brittle to extrude as monolayer films, but coextruded films of 50% core layers of the blends with 25% skin layers of PP (Basell SA-861) were produced.

Results:

Blends

Physical properties of the blends were measured by Rheteeh (Table 4). The PP-COC blends did not combine well. (Consideration of the higher MI COC grade represents an unsuccessful approach to overcoming the mixing problem.) As the elongation, impact and modulus values summarized here all suggest, the PP-COC nanocomposites as produced became very brittle.

TABLE 4
PP/MLS and PP-COC/MLS Blends by Rhetech:
Physical Properties

Property→	*Specific Gravity*	*Tensile @Yield*	*Elongation @Yield*	*Flexural Modulus*	*IZOD Impact*	*HDT*
Sample↓		psi	%	kpsi	ft-lb/in	°F
5462J	.926	4600	11.0	192	.87	188
5467J	.935	4640	11.0	200	.95	194
5468J	.996	5950	1.9	396	.24	246
5470J	1.006	5920	1.8	408	.24	244
5473J	1.000	5950	2.2	365	.27	250
5476J	1.007	7180	3.2	388	.31	252

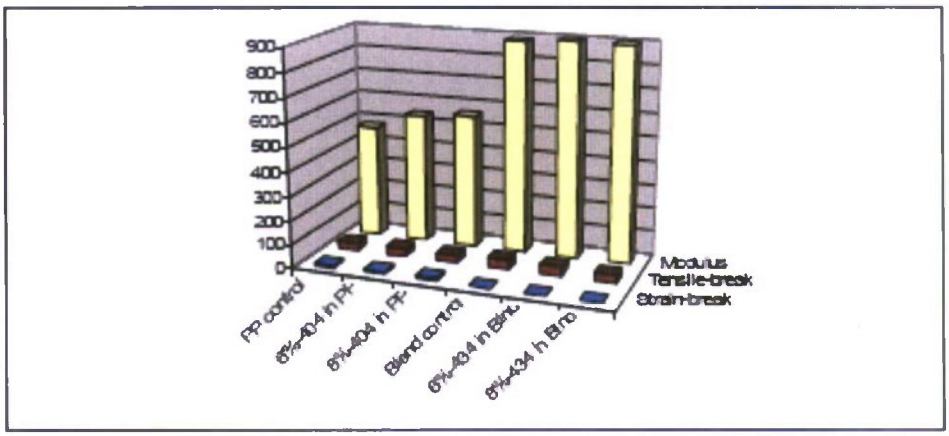
CPP+COC blend (indications of heterogencity of the polyolefins were observed.) The nanocomposite with the grade 404 appeared more darkly-colored sample duc to the particular formulation of this nanoclay, which additionally exhibits UV protection (all NBM patent pending technology). Inorganic clay content was measured by a TGA Q500 (TA Instruments). Samples were heated from 30° C to 80 °C at a rate of 10° C/min in a N_2 atmosphere. All experimental values were reasonably close to calculated ones.

OTR (Oxygen transmission rate) measurements were performed in duplicate at 21°C and 80%RH in 450 micron thick specimens. The lowest permeability value attained is quoted. Equipment used was an Oxtran 100 with humidity control from MOCON. On the basis of OTR testing summarized in Table 5, two nanocomposites were selected for additional production and film extrusion. General mechanical properties of the NBM blends also indicated that the COC/PP blends were brittle (Figure B).

TABLE 5: PP/MLS and PP-COC/MLS Blends by NBM:
Physical Properties

Test Value	nominal clay	TGA clay	O_2 Barrier improvement
Units→	%	%	%
PP/clay samples ↓			
9022401 (PP only)	0	–	–
9022403	8	8.2	13.9
9040101	8	8.5	-19
9040102	8	8.4	1.7
9051202	8	7.9	-4.9
9051302	4	4.3	-4.0
Blend/clay samples ↓			
9022404 (blend only)	0	–	–
9022406	8	8.1	-60.1
9030603	8	8.3	9.2
9040103	8	8.4	-23.8
9051201	8	8.3	-3.6
9052601	8	8.1	33.8

Figure B: Physical properties of NBM blends



Films:

The WVTR of all six films with Rheteeh blends were evaluated (Table 6). Schirmer et al. (2008) reported the WVTR of that PP/MLS cast film was 43% lower than a neat PP. Comparable commercial cast PP films produced by Printpack provide WVTR of 12.4 gm/m² day/25 mm, suggesting that the Rhetech PP/MLS blends (at both 6% and 8% MLS) achieved less than a 15% improvement. In coextruded form, however, the PP/COC-MLS blends sandwiched between PP skin layers provided nominal reductions of 35-44%

Table 6: Barrier Results Rhetech Blends

No.	Film Type	Layer 1 (25%)	Layer 2 (50%)	Layer 3 (25%)	WVTR/25μ gm m² •day	Description of Rhetech Blend
1	Mono	5462J	5462J	5462J	10.71	6% clay in PP
2	Mono	5467J	5467J	5467J	11.34	8% clay in PP
3	Coex	SA-861	5468J	SA-861	7.87	6% clay in Hi MI blend
4	Coex	SA-861	5470J	SA-861	6.93	8% clay in Hi MI blend
5	Coex	SA-861	5473J	SA-861	7.72	6% clay in Lo MI blend
6	Coex	SA-861	5476J	SA-861	8.04	8% clay in Lo MI blend

Similarly, WVTR of the film made with NBM blend are presented in Table 7. Neither blend could be extruded as a monolayer film becausc of the buildup of clay particles on the die lips. To avoid this effect, PP/COC/"corc"/COC/PP coextrusions were fabricated. Thc PP/COC/Clay blend (E09052601) proved too brittlc for even this approach. In one casc, PP was uscd as thc corc; the othcr uscd the NBM: "E09022401".

The WVTR of the coex with the NBM PP/clay blend was lower, but not significantly so (P=0.95.) With a core layer of only about 20μ, such a difference may be difficult to establish without more data.

Industry values for the barrier of PP and COC 6013F-04 are 10.17 and 5.23 gm/ m² per 25 μ respectively (Jester, 2008.) For a four mil coex with 67% PP and 33% COC, thesc values imply a barrier of 1.94 (gm/m² pcr 100 μ). This is in reasonable agreement with the experimental valuc of 1.41 (gm/m² per 100 μ). It also suggests that thc transmission rate of a 100 μ coextrusion of PP/COC/PP/COC/PP would be 24% lower than a cast PP sealant of the same thickness. Although the difference is not enough to completely bridge the gap between the DOD WVTR specification and experimental results, it could contribute to a satisfactory structure if other water vapor barrier improvements were implemented.

Table 7: Barrier Results NBM Blends

No.	Film Type	Layers COC= Topas 6013F-04)					WVTR/film	Description of Core (Layer 3)
	Out/in	1	2	3	4	5	gm/m²•day (s.d.)	
	(%)	22	17	22	17	33		
1	PP Coex	PP	COC	PP	COC	PP	1.41 (0.08)	PP: "Basell SA-861"
2	Blend Coex	PP	COC	NMB	COC	PP	1.18 (0.00)	NBM: "E09022401"

Discussion:

Clearly, the attempt herc to establish synergistic cffects among the separatc water barrier functionality of PP, COC and MLS nanocomposites failed. The lack of miscibility of PP and COC apparently excludes the kind of dense, non-polar polymeric matrix necessary to slow the diffusion of water molecules through such blends. The significant out-of-plane shape of both polymers pos-

sibly presents so much steric hindrance that such blends may be difficult to achieve at any relative proportions that otherwise might suggest improved WVTR performance.

However, the PP/nanocomposite blends, even if incorporated into coextruded films with integral PP skin layers on either side, do suggest enhanced water vapor barrier performance compared to neat PP films. Similarly, coextruded films with PP layers and COC layers indicate enhanced water vapor barrier performance compared to neat PP films.

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Annex 7. Dielectric Properties of Flexible Packaging Materials

Abstract: This study investigated the dieleetrie properties of various all-plastic, high barrier flexible paekaging films under eonsideration for use with a microwave thermal sterilization process. The process seeks to provide mierobiologieally safe entrée produets in flexible pouches capable of supporting 3 year shelf life of the entrees stored at 27°C (80°F). Product protection prerequisites for this objective require that the flexible packaging films funetion to provide oxygen, moisture, and light barrier. The films were assessed by a special resonance eavity and network analyzer. The results indieate that the teehnique provides a means of quantitative evaluation of the suitability of various flexible packaging materials for microwave sterilization

Key words: dieleetric properties, barrier films, microwave, sterilization, flexible packaging

Background: Well defined concepts deseribe the interaction of electromagnetic (EM) energy with any material (Datta and Amantheswaran, 2001). Three key terms deseribe the eonversion of sueh energy into thermal energy (e.g. microwave heating):

Dieleetric Constant[3]:	**ε'**	the ability of a material to absorb energy
Dielectric Loss Faetor:	**ε''**	the ability of a material to eonvert absorbed EM energy into heat
Loss Tangent:	**Tan δ=ε''/ε'**	a measure of the rate of heating resulting from EM energy absorption

Heating in a microwave sterilization process primarily results from oscillations of ionic and dipolar moleeules as they couple with the frequency of the microwave energy. Similar molecules in packaging materials can also couple with the microwaves. In doing so, the energy of the mierowave raises the temperature of the packaging and becomes unavailable to heat the food in the paekage exeept through eonductive heat exchange.

Many polymers eommonly used in flexible packaging films, particularly polyolefins, themselves have relatively low dieleetric eonstants (i.e. they act as insulating materials.) Others (e.g. condensation polymers such as polyesters and polyamides) have higher dielectric constants. Additives and eoatings on any such films refleet a wide range of eonstants, depending on their chemical composition. In partieular, "photo-opaque" flexible packaging material historieally has used earbon black at concentrations up to 50% in a given layer as a light barrier material. This material has a large dielectric constant, causing its use as the light barrier filler in high barrier flexible packaging films to reduce the effieiency and throughput of a microwave sterilization process. Nano-scale clay platelets

[3] The Institute of Electrical and Electronics Engineers (IEEE), prefers the term "relative static permittivity" over "dielectric constant," because of ambiguous uses of the term in early reports. As used here, the "absorbance" of the EM energy refers to the excitation of atoms in a material's molecular structure in response to the magnetic and/or electric flux of the energy. Energy so "absorbed" is unable to reflect from or transmit through the material. Food science literature continues to use the term "dielectric constant", and so it is applied in this report.

exfoliated in polymers to increase water vapor and oxygen barrier also have large dielectric constants and are likely to cause similar inefficiencies.

The objective of this research is to adapt existing methods for dielectric property measurements of food systems for thin (~250 μ) films, and to quantify the dielectric constants of multi-layered alternative light barrier options for high barrier flexible packaging films. Such quantified properties can help guide materials selection and predict microwave sterilization process efficiency for a specific packaging material.

After researching the options for measurement of very thin low loss materials the best system setup was found to be a resonance cavity made by QWED (Warsaw, Poland) in conjunction with a ENA series network analyzer (Agilent Technologies, Santa Clara, US). Two samples of plastic were sent to QWED for preliminary evaluation in the resonance cavities. Initial results were satisfactory. Additional tests over different frequencies and with several layers of film were asked to be performed by QWED to confirm suitability of resonance cavity technique for measurement of dielectric properties of plastic films. Results were satisfactory.

Materials and Methods: Guan et al. (2004) measured the dielectric properties of mashed potatoes in anticipation of developing a microwave sterilization process for this and other food systems. Samples were stored at 4°C and conductivity was measured within 48 h using a conductivity meter (CON-500, Cole-Parmer Instrument Co., Vernon Hills, IL, U.S.A.). Dielectric properties were measured over a frequency range from 1-1800 MHz and a temperature range from 10°C-130°C using an open-ended coaxial-line probe method. The system was composed of an RF impedance analyzer with a calibration kit (4291B, Agilent Technologies, Palo Alto, CA, U.S.A), a custom-built test cell (20mm inner diameter, 94mm height), a high-temperature coaxial cable, a dielectric probe kit (85070B, Hewlett Packard Corp., Santa Clara, CA, U.S.A), and an oil bath equipped with a programmable circulator (Model 1157, VWR Science Products, Westchester, PA, U.S.A).

The samples were placed into the test cell and the dielectric probe was sealed in close contact with the samples, which was maintained using pressure from a stainless steel spring and piston. The calibration and measurement procedure has been previously given by Wang et al. (2003). Following calibration, each sample was measured at 201 discrete frequencies in the range of 1-1800 MHz at 20°C, 40°C, 60°C, 80°C, 100°C and 120°C. Measurements were run in triplicate and mean values and standard deviations were calculated.

The ENA series network analyzer E5071 (Agilent Technologies) with the split post resonance cavity at microwave frequency rang 2.6 GHz (QWED, Warsaw, Poland) are used to perform the data acquisition (Fig. 1.1 and 1.2). The 85071E Material measurement software with a cavity option 300 is used to calculate the dielectric properties of the thin plastics. Films were cut to the required dimensions of about 85mm × 90mm and inserted into the cavity for measurement.

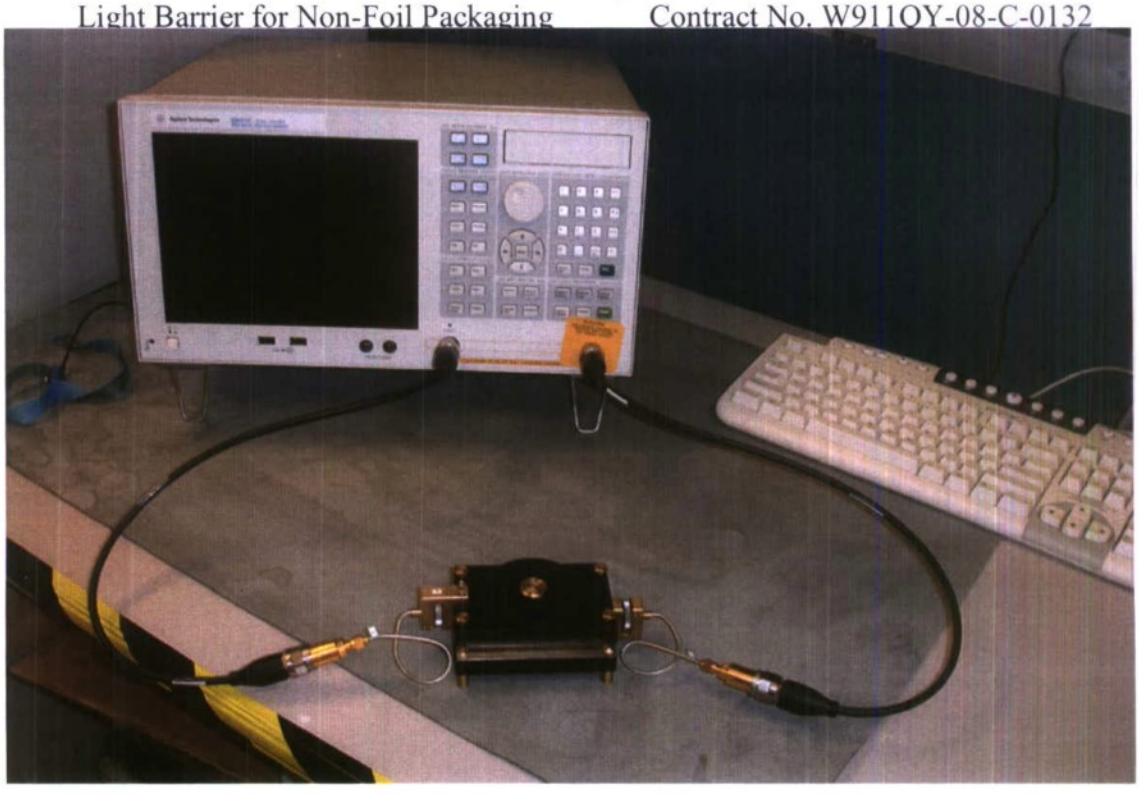

Figure 7.1 Network analyzer and split resonance cavity setup.

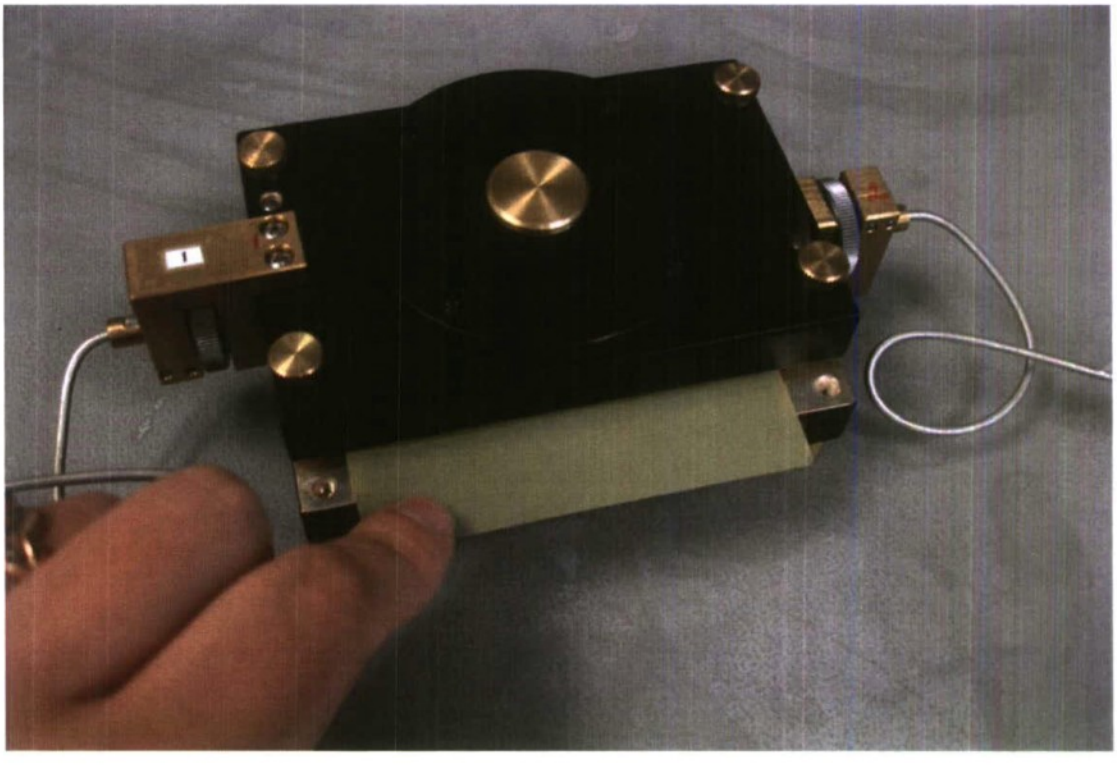

Figure 1.2 Detail: Split resonance cavity setup.

Film thickness was measured at 5 different points on the films using a digital caliper (Mitutoyo) with 0.01mm resolution (for Table 1 data), and also using an electronic disk micrometer (SPI) with resolution of 0.001mm (for Table 2 data). The average of 5 measurements was used.

Measurements were done on three individual films, on 2 layers and 3 layers of film. The average of all measurements was used. For the most film structures the dielectric properties data for single layer and 2-3 layers were close. Thickness of the film is important parameter for the measurements since the error of thickness measurement is directly proportional to the error of dielectric properties.

High barrier flexible packaging films supplied by Printpack are summarized in Table I. A pigmented adhesive provided significant light barrier (300nm to 700nm) for these laminations.

Table I: Printpack Barrier Laminations

No.	Structure	Comment
1	OPET/BON/Al Foil/CPP*	Control
2	OPET/Kurarister C/Kurarister N/CPP	Best technical candidate
3	Kurarister C/ CPP	Test Kurarister C
4	Kurarister N/ CPP	Test Kurarister N
5	GL-ARH/EVOH-N-PP Coex	Test GLARH for WVTR
6	OPET/Mx-PPCoex	Test MxD6 for OTR
7	OPET/I-PP Coex	Test "Imperm"
8	Kurarister C/ nanoPP2-COC Coex	Test Kurarister C with WVTR plus
9	Kurarister C/ nanoPP1	Test Kurarister C with WVTR plus
10	Kurarister C/ nanoPP2	Test Kurarister C with WVTR plus

***KEY**

BON .....Biaxially oriented nylon-6
COC .....polynorborene (cyclic olefin copolymer)
COC coex.....25µ P/50µ P-COC-nano/25µ P
EVOH .....32 mol.% ethylene vinyl alcohol copolymer
I .....MxD6 Nylon nanocomposite ("Imperm")
GL-ARH .....Aluminum oxide coated OPET (Tanaka and Sasaki, 2009
Kurarister C ...Proprietary coated OPET (Nakamae,2009)
Kurarister N ...Proprietary coated BON (Nakamae,2009)
Mx.....MxD6 Nylon
N Nylon-6
nano.....Montmorillonite clay modified with a 4° ammonium salt
nanoPP1 .....6% nano-PP blend
nanoPP2 .....8% nano-PP blend
OPET .....Oriented polyethylene terephthalate
P (CPP) .....Polypropylene